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Gas Adsorption Studies in Metal-Organic Frameworks

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Abstract

This thesis describes the synthesis of a novel highly stable metal-organic framework, NOTT-300(Cr), as well as the synthesis of three new mixed metal analogues of NOTT-300 using different compositions of aluminium and chromium. These new MOFs were used in gas sorption experiments to investigate potential selectivity and uses for gas stream separations with particular focus on CO₂ and C₂ hydrocarbons. The gas adsorption properties of NOTT-300(Al) for CO₂ and C₂ hydrocarbons are also investigated in detail.

Chapter 1 – An introduction to MOFs, including their synthesis and various applications along with examples from the literature is discussed. The potential application of MOFs for difficult industrial separations is considered and a brief background on CO₂ and climate change is discussed along with the current issues facing carbon capture technologies. The uses of C₂ hydrocarbons and their difficult separation are also assessed.

Chapter 2 – A novel Cr(III) containing analogue of NOTT-300 has been successfully synthesised (NOTT-300(Cr)) and the structure solved from the PXRD pattern. The gas adsorption properties, with specific focus on CO₂ uptake and selectivity, are described and compared with those obtained for NOTT-300(Al). The CO₂ adsorption in NOTT-300(Cr) was further probed using *in situ* gas loaded PXRD studies. Flow experiments were used along with IAST calculations to assess and compare the CO₂/CH₄ and CO₂/N₂ selectivity in NOTT-300(Cr) and compared with NOTT-300(Al). Although the CO₂ adsorption capacity is higher for NOTT-300(Cr) than for NOTT-300(Al) (10.1

vs. 9.5 mmol g^{-1} at 273 K and 20 bar), the CO_2 selectivity is lower due to an increased adsorption capacity for other gases such as CH_4 .

Chapter 3 – A mixed metal NOTT-300 series containing varying amounts of Al and Cr, *i.e.* NOTT-300(AlCr2:1), NOTT-300(AlCr1:1) and NOTT-300(AlCr2:3), was synthesised in order to further probe the effect of the metal content on the CO_2 adsorption and selectivity of this framework. Each of the materials show high CO_2 adsorption capacity, however, there appears to be no specific trend in adsorption properties with respect to metal ratio. The CO_2 adsorption and selectivity in NOTT-300(AlCr2:1) was further investigated using dual component adsorption isotherms and *in situ* gas loaded PXRD and IR studies. The three different -OH groups present in the mixed metal materials form interactions of differing strength with the CO_2 molecules, explaining the different adsorption properties across the series. The mixed metal series displays higher CO_2 adsorption than NOTT-300(Al), but lower CO_2 selectivity. When compared to NOTT-300(Cr) the CO_2 adsorption of the heterometallic series is lower but the selectivities are comparable.

Chapter 4 – The adsorption of C_2 hydrocarbons and possible C_2 separations and C_2/C_1 separations are investigated and compared in the NOTT-300 materials described in this thesis. All frameworks display considerably higher adsorption capacity for C_2 hydrocarbons vs. CH_4 . However, the potential for C_2 separations was more varied, with NOTT-300(AlCr1:1) showing moderate $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ selectivity (2.7:1), while the calculated selectivity for NOTT-300(Cr) was negligible (1:1). NOTT-300(Al) was used in breakthrough experiments to assess the separation capability of two different hydrocarbon mixtures ($\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$).

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List of Publications

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List of Abbreviations

°	Degree
1D	One dimensional
3D	Three dimensional
Å	Angstrom
ABR	Automated breakthrough reactor
ATR	Attenuated total reflectance
BET	Braun Emmett Teller
C	Celsius
cif	Crystallographic index file
cp	Closed pore
DECC	Department of energy and climate change
DFT	Density functional theory
DLS	Diamond light source
DMF	Dimethylformamide
dobdc	2,5-dioxido-1,4-benzenedicarboxylate
<i>ee</i>	Enantiomeric excess
HOF	Hydrogen-bonded organic framework
IAST	Ideal adsorbed solution theory
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IGA	Intelligent gravimetric analyser
INS	Inelastic neutron scattering
IPCC	International panel on climate change
IR	Infrared
K	Kelvin
lp	Large pore
M	Metal
MEA	Monoethanolamine
MeOH	Methanol
MFC	Mass flow controller
MMOF	Microporous metal organic framework
MOF	Metal organic framework

MRI	Magnetic resonance imaging
NMOF	Nano-metal organic framework
np	Narrow pore
pcaH	Pyrazine-2-carboxylic acid
PTFE	Polytetrafluoroethylene
PXRD	Powder X-ray diffraction
S.A	Surface area
SBU	Secondary building unit
TGA	Thermogravimetric analysis
ZIF	Zeolitic imidazolate framework

Chapter 1 – Introduction

1.1 Metal-Organic Frameworks (MOFs)

1.1.1 What are Metal Organic Frameworks?

Metal-organic frameworks (MOFs) are a class of hybrid compounds that are constructed from single metal ions or clusters bridged by multi-dentate organic ligands (Fig. 1.1). These materials tend to form 3D networks with cages or channels and often show permanent porosity after activation, *i.e.* there is no sample decomposition. It is the porous nature of MOFs, along with their thermal and chemical stability, that make them such a popular area of research for a wide range of applications such as drug delivery,¹⁻⁶ catalysis,⁷⁻¹³ chemical sensors,¹⁴⁻¹⁹ proton conductivity,²⁰⁻²³ extraction^{24,25,26} and gas separation²⁷⁻³⁰ and storage.³¹⁻³⁴ The structure of MOFs can be fine-tuned to suit a specific application through careful choice of the metal ion and organic ligand used.³⁵⁻³⁸ There are two possible “reactive” sites found within a framework, the first is the ligand, *i.e.* introduce polar functional groups to enhance interactions, or Lewis acid/base sites for catalysis and the second possible interactive site is at the metal ion.

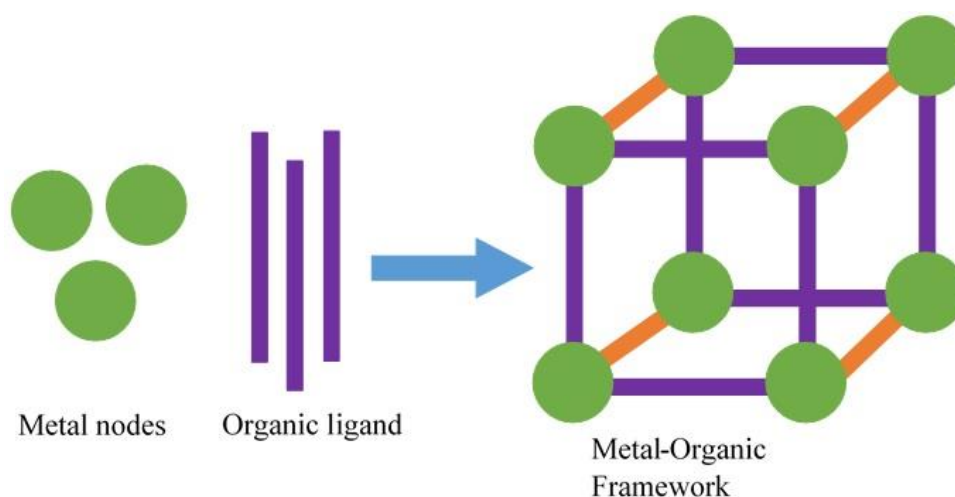


Fig. 1.1 Schematic representation of the assembly of a MOF. Orange bonds represent different M-M connectivity, such as -OH or -O.

One of the first successfully synthesised MOFs that retained its 3-dimensional structure and porosity after activation was MOF-5, reported by Yaghi *et al.*³⁹ MOF-5, $\text{Zn}_4\text{O}(\text{BDC})_3$ (BDC – 1,4-benzenedicarboxylate), consists of a Zn acetate cluster, $\text{Zn}_4\text{O}(\text{CO}_2)_6$, connected along the orthogonal axis by the phenyl ligand (Fig. 1.2a). It was found that the rigidity of the ligand and metal cluster (the secondary building units (SBUs)) helped to keep the porous nature after the removal of solvent from the pores. This first promising result led to an entire isorecticular series to be synthesised (IRMOFs) with differing functionalities on the phenyl ligand and different lengths of ligand to investigate how these changes affect the properties of the IRMOFs.⁴⁰ It was found that the introduction of hydrophobic groups increased the capacity for CH_4 adsorption in these materials, with IRMOF-6 (Fig. 1.2b) reaching an uptake of 240 cc g^{-1} at 298 K and 36 atm. However, it was also found that increasing the length of the ligand is just as likely to lead to interpenetration (IRMOF-9, -11) as it is to lead to a larger pore aperture/cavity (IRMOF-8, -16).

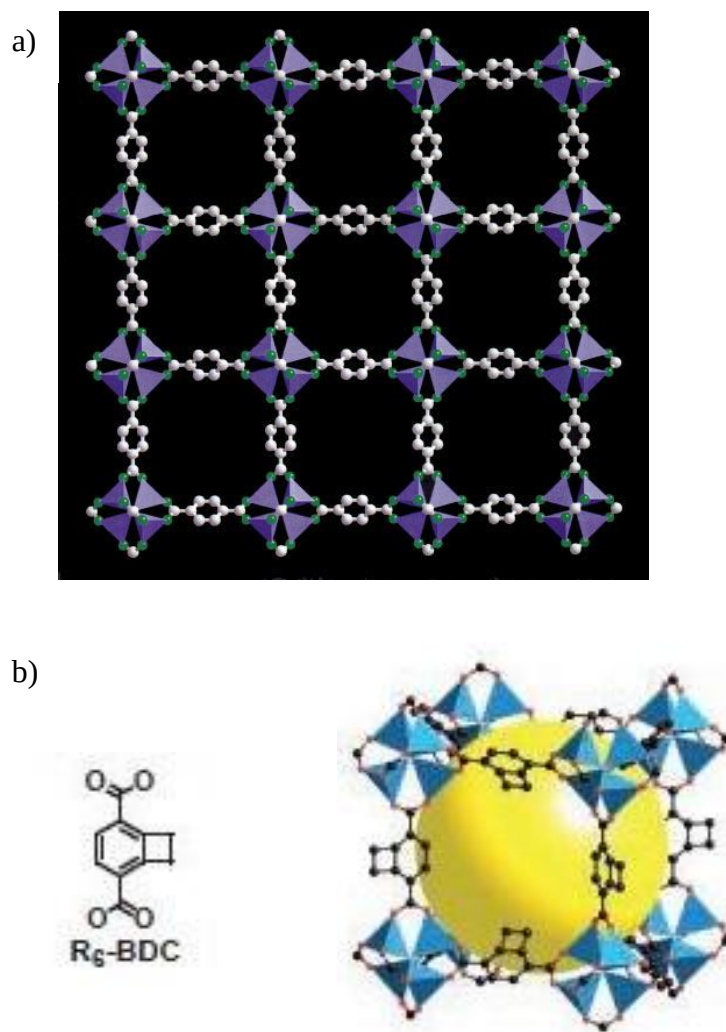


Fig. 1.2 a) Crystal structure of MOF-5. Figure taken from reference 39. **b)** Structure of the ligand R₆-BDC and the resulting crystal structure of IRMOF-6. Figures taken from reference 40.

There has been a large amount of work carried out into understanding the fundamentals of MOF-5, its synthesis^{41,42,43} and properties.^{44,45} There have also been several studies conducted to investigate how guest species diffuse within the framework, these have been probed computationally⁴⁶ as well as with NMR,⁴⁷ IR⁴⁸ and neutron spectroscopy.⁴⁹ MOF-5 is a good candidate for these types of experiments as the ligand has a small number of H atoms and so can be easily investigated by neutron spectroscopy and H NMR. Owing to the success

of these methods with MOF-5 they are now commonly used with many other MOFs such as HKUST-1,⁵⁰ NOTT-300(Al)⁵¹ and MOF-74.⁵²

1.1.2 Construction of MOFs

The choice of ligand when synthesising a MOF for a targeted application is very important as different functionalities, geometries and sizes are available. A large number of ligands described in the literature contain a core consisting of aromatic rings, because of their rigidity which allows the material to retain its porosity after solvent removal.⁵³ There are also different metal-binding moieties to consider, a common one frequently used in MOFs is the carboxylate group which forms strong bonds with a range of metal centres and are generally easy to synthesise.^{54,55} Phosphonate groups are also used, however, they present difficulties during the MOF synthesis often forming layered structures with limited porosity.⁵⁶ There are many more functional groups reported in the literature, including mixed moiety ligands. There is an extensive series of compounds called zeolitic imidazolate frameworks (ZIFs) constructed using imidazolate ligands with transition metals; they show high thermal stability and moderate gas adsorption uptakes (Fig. 1.3).^{57,58,59} Different functional groups can be incorporated into the MOF structures through the choice of ligand used. Specific functionalities can be chosen to increase favourable interactions with adsorbed species, *e.g.* H-bond donor or acceptor atoms, Lewis acid or base sites. The size of the ligand also impacts on the framework structure and properties, for example a long ligand will likely lead to a MOF with larger channels and pores allowing for increased adsorption of a gas but can also lead to interpenetration resulting in a denser structure.⁶⁰⁻⁶³

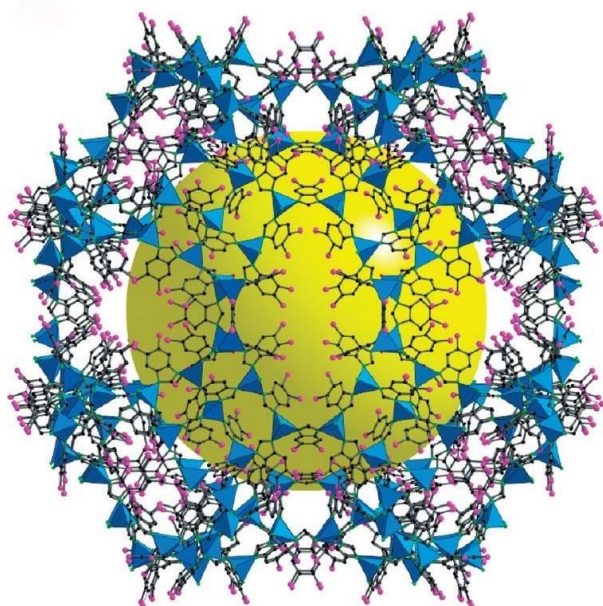


Fig. 1.3 Crystal structure of ZIF-100, constructed from Zn(II) and an imidazolate ligand. Figure taken from reference 57.

There are many different metal ions that have been used in MOF synthesis that lead to materials with differences in structure and properties. The building blocks of a MOF are sometimes described as secondary building units (SBUs) with different metals having a tendency to form different SBUs. For example Cu(II) often forms tetragonal Cu-paddlewheel units⁶⁴ $\text{Cu}_2(\text{COO})_4$ whilst Zr(IV) tends to form square anti-prismatic $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{RCO}_2)_8$ clusters,⁶⁵ Fig. 1.4. As previously mentioned the metal node can also be a site of interaction with an adsorbed species; some SBUs (including Cu-paddlewheel units) can be desolvated to generate open metal coordination sites which can bind adsorbed gas molecules or act as a catalytic centre for chemical reactions.

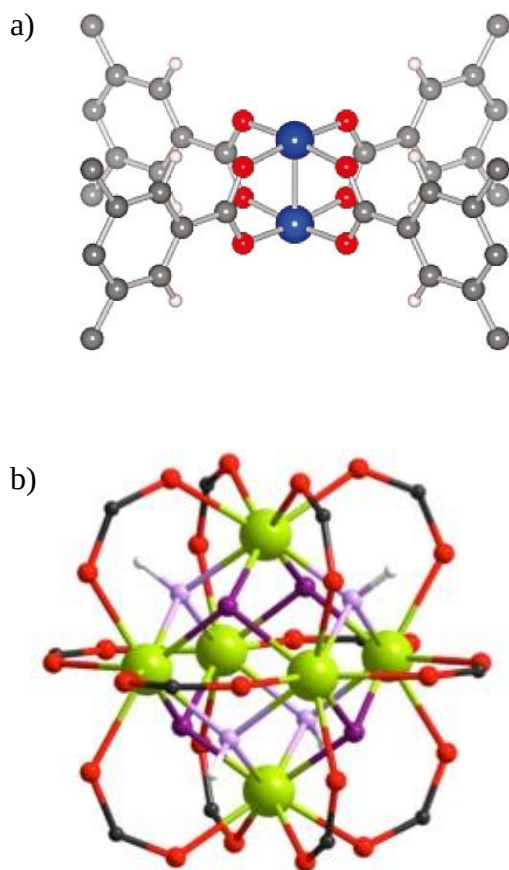


Fig. 1.4 a) Cu(II) paddlewheel SBU with axial solvent molecules removed. Figure taken from reference 66. b) $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{RCO}_2)_8$ SBU. Figure taken from reference 67.

1.1.3 MOF Synthesis

MOFs are often synthesised *via* a self-assembly process using solvothermal reaction conditions, meaning heating at high temperature in a sealed system leading to high pressures.⁶⁸ Because of the elevated pressure the reactions are often carried out in either PTFE lined steel autoclaves or thickened glass pressure tubes. The metal source is commonly soluble metal salts such as nitrates, chlorides and acetates. In cases where the ligand has reduced solubility in the reaction media the pH is adjusted to more acidic reaction conditions to aid in the self-assembly process. There are many factors that affect the outcome of synthetic reactions of a MOF, such as the pH of the reaction medium, duration,

temperature, concentration and reagent stoichiometry. After a MOF has been synthesised, before it can be used in any application, it requires activation: all the solvent in the internal porous space is removed leaving a completely empty framework. This then makes the space available for the desired substrate. Owing to the wide range of potential applications that MOFs can be used for their popularity has increased dramatically over the last decade, Fig. 1.5.

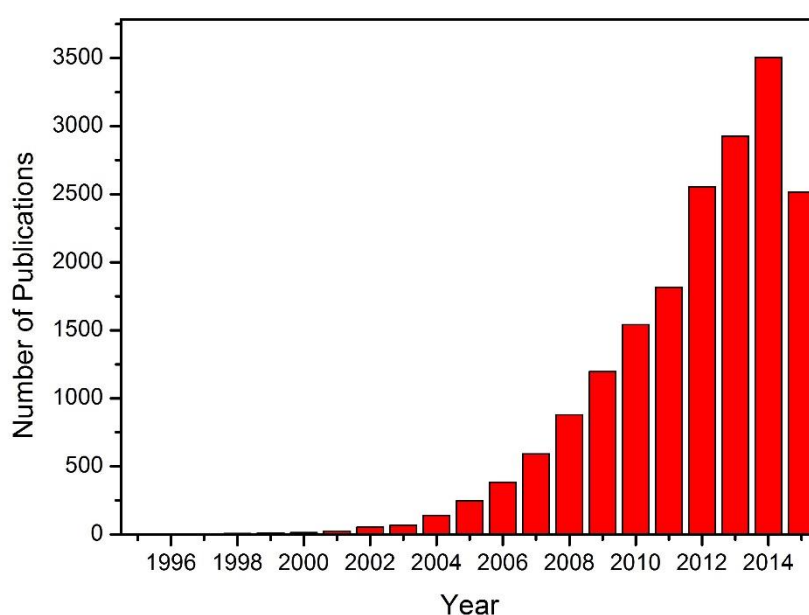


Fig. 1.5 A graph to show the trend in MOF publications over the past two decades, based on SciFinder search results for Metal-Organic Frameworks and MOF.

1.1.4 MOFs in Pharmaceuticals

MOFs have been developed in the pharmaceutical industry for uses including carrier systems and as magnetic resonance imaging (MRI) contrast agents.^{69,70,71}

The low sensitivity of MRI often requires the contrast agents to be administered in high doses. The ability to tune the structures of these frameworks could lead to MR enhancing nanoscale-MOFs (NMOFs) that are more suitable to be used

in higher doses owing to their biocompatibility and low toxicity. Taylor *et al.* reported that by functionalising the surface of the Mn(II) MOFs $[\text{Mn}(\text{BDC})(\text{H}_2\text{O})_2]$ and $[\text{Mn}_3(\text{BTC})_2(\text{H}_2\text{O})_6]$ (BDC – 1,4-benzenedicarboxylate, BTC – 1,3,5-benzenetricarboxylate) with a fluorophore and a cell-targeting peptide they could enhance the delivery of the agent to the cancer cells.⁷²

Carrier systems are used to improve the activity for known molecules by either increasing efficiency or decreasing toxicity. Crucially they have to be biocompatible in order to be viable agents. Horcajada *et al.* investigated the use of MIL-53 in delivery of ibuprofen.⁷³ This particular MOF was chosen for study as it exhibits “breathing” type flexibility: the pore sizes and shape can change upon uptake of guest species. Both MIL-53(Cr) and MIL-53(Fe) were studied and it was shown that the flexibility enhances controlled release of pharmacological molecules (Fig. 1.6). Both MIL-53(Cr) and MIL-53(Fe) adsorbed 20 wt% of ibuprofen showing that the adsorption mechanism does not depend on the metal centre. In this instance MIL-53(Cr) could not be used in biological application as it is toxic.

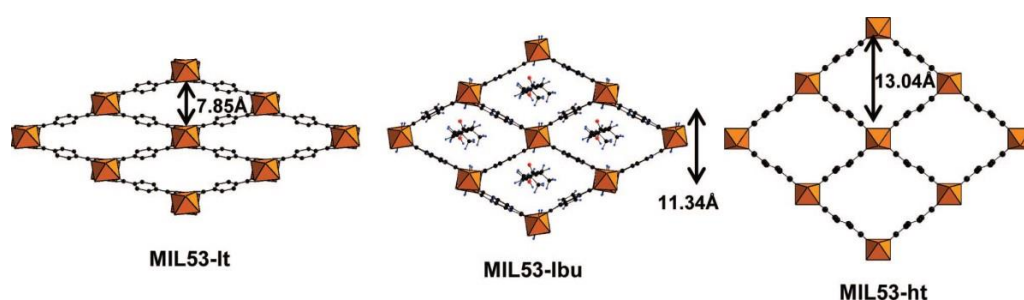


Fig. 1.6 Schematic representation of the breathing effect of MIL-53(Cr) upon dehydration/hydration and adsorption of ibuprofen. Figure taken from reference 73.

1.1.5 MOFs in Catalysis

The drive to create homochiral porous MOFs has increased because they are highly attractive for asymmetric catalysis. Catalytically active MOFs combine various advantages of both heterogeneous and homogeneous catalysts.⁷⁴ Advantages to this approach include the facile recovery and reuse of the catalyst and the reduced contamination in the products caused by catalytic residues.⁷ The first use of a MOF in catalysis was reported in 1994 by Fujita *et al.*⁷⁵ They reported the synthesis of a Cd framework with the ligand 4,4'-bipyridine, giving a material with the overall formula $\{[\text{Cd}(4,4'\text{-bpy})_2](\text{NO}_3)_2\}$. It was reported that this framework structure promoted cyanosilylation of aldehydes. Much more work has been conducted in this area; a timeline of significant milestones is outlined in Fig. 1.7.

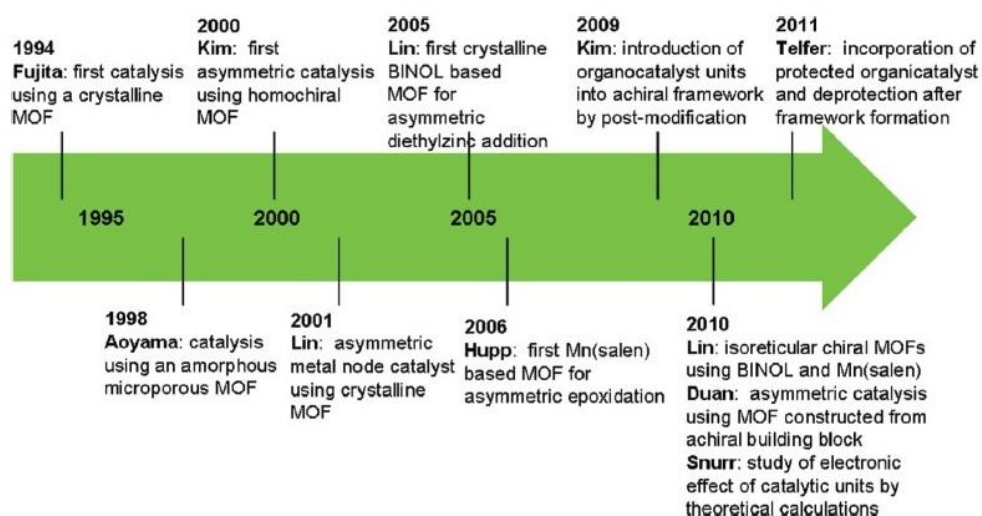


Fig. 1.7 Timeline of MOFs used in catalysis. Figure taken from reference 76.

The first use of a homochiral MOF, D-POST-1, in asymmetric catalysis was reported by Kim *et al.* in 2000.⁹ D-POST-1 was synthesised from D-tartaric acid (**1**) and a source of Zn^{2+} to give an empirical formula of $[\text{Zn}_3(\mu_3\text{-O})(\text{1-H})_6]\cdot 2\text{H}_2\text{O}\cdot 12\text{H}_2\text{O}$ with large chiral channels running along the direction of the *c* axis. The catalytic activity of POST-1 for transesterification of

2,4-dinitrophenyl acetate with a large excess of racemic 1-phenyl-2-propanol was investigated. Both L and D-POST-1 produce the corresponding esters with 8 % enantiomeric excess (*ee*). Although the *ee* is not high it is still a pivotal result as it was the first case of asymmetric induction by modular porous materials.

Another use of MOFs in catalysis was reported by Wu *et al.* in which a homochiral cadmium containing framework was synthesised using a chiral bridging ligand, (R)-6,6'-dichloro-2,2'-dihydroxy-1,1'-binaphthyl-4,4'-bipyridine.⁷⁴ The resulting framework contained 1D zigzag [Cd(μ -Cl)₂] chains bridged by the ligands to create a non-interpenetrating structure with accessible pores.

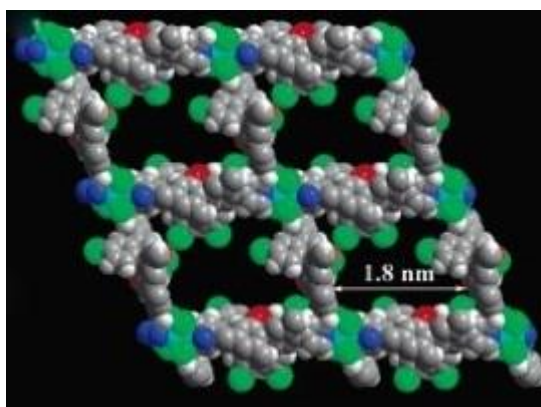


Fig. 1.8 Crystal structure of [Cd₃Cl₆L₃] using space filling model, viewed down the *a* axis showing the large chiral channels. Figure taken from reference 74.

The framework was post synthetically treated with excess Ti(O^{*i*}Pr)₄ to introduce the catalytically site. After treatment the material was found to catalyse the addition of ZnEt₂ to a range of aromatic aldehydes with comparable conversion and *ee* to that of a homogeneous analogue (BINOL/Ti(O^{*i*}Pr)₄). In particular, the addition of ZnEt₂ to 1-naphthaldehyde afforded the desired product with complete conversion and 93 % *ee*.

1.1.6 MOFs Applications in Gas Storage

The use of H₂ as a fuel is an ideal solution to the green energy problem as it can potentially achieve zero carbon emission at the point of use.⁷⁷ However, there are a range of technical problems facing efforts to use hydrogen as an alternative energy source. The storage of H₂ as compressed gas or liquid causes significant difficulties due to the high pressure (>200 bar) or low temperatures (~20 K) required. A large amount of research is being conducted to find a more economically and technically viable solution for the storage of H₂, focussing in particular on porous materials.^{78,55} The extremely high surface areas of some MOFs make them ideal candidates for storing H₂. The adsorption isotherms of H₂ are currently measured at 77 K, the low temperature is unsuitable for real world applications therefore this needs to be addressed.

Schröder *et al.* investigated the H₂ adsorption in the MOF NOTT-112 which was synthesised using a hexacarboxylate ligand, 1,2,5-tris-(3',5'-dicarboxy[1,1'-biphenyl]-4-yl) benzene and Cu(NO₃)₂.3H₂O.⁶¹ It was found that increasing the ligand size increased the pore volume but this is limited by the onset of framework interpenetration. The 3D framework of NOTT-112 can be viewed as tessellation of three types of polyhedral cages (Fig. 1.9a). High pressure H₂ adsorption isotherms were measured from 0-80 bar at 77 K and show a maximum excess uptake of 7.07 wt% at 40 bar. The total H₂ uptake was calculated using the pore volume derived from the N₂ isotherm and the H₂ density at different pressures. This value was calculated to be 10.0 wt% at 77 bar. NOTT-112 has a combination of large pores and high surface area within a rigid framework: the enhanced H₂ adsorption suggests that this mixture of small and large polyhedral cages is a powerful strategy to optimise H₂ uptake at high pressures.

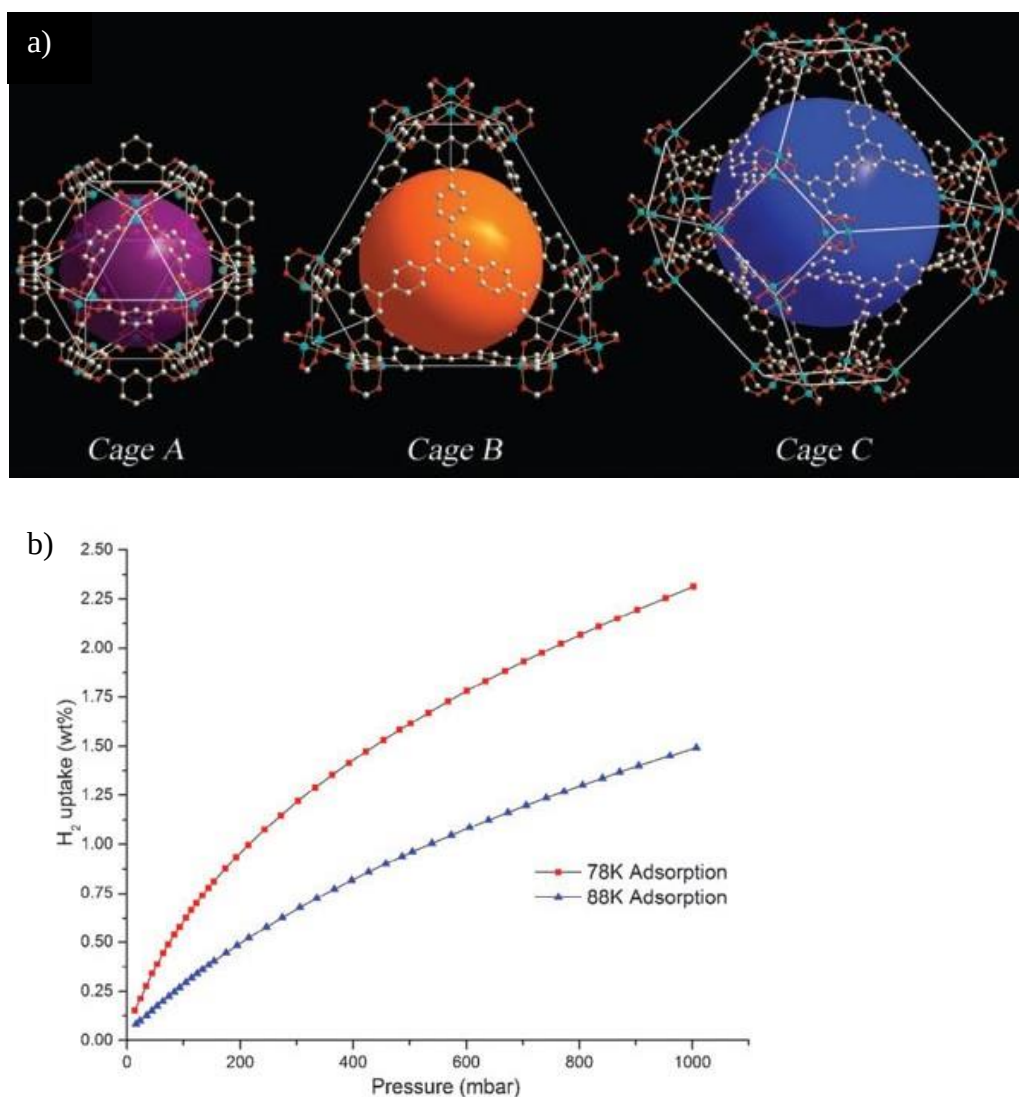


Fig. 1.9 **a)** Different cages in the crystal structure of NOTT-112. **b)** H₂ adsorption isotherms in NOTT-112 at 78 and 88 K. Figures taken from reference 61.

There are several proposals to increase H₂ adsorption uptake in MOFs. One such theory suggests that doping the framework with Li can increase the H₂ adsorption owing to the strong affinity of Li⁺ for H₂.⁷⁹ Xiang *et al.* investigated this principle by doping two well-known MOFs, MIL-101(Cr) and Cu₃(BTC)₂, with lithium naphthalenide.⁸⁰ The PXRD patterns of the Li doped MOFs match the unadulterated MOFs suggesting that the additional Li does not disturb the structure or destroy the crystallinity. The BET surface area of both materials was

reduced after the doping process and it is thought that the Li may occupy the micro-pores in the framework. The H₂ uptake in Cu₃(BTC)₂ is 2.41 wt% and after doping with Li this increased to 3.5 wt%. The H₂ uptake in MIL-101 (Cr) also increased from 2.37 wt% to 3.39 wt% after doping with Li. Despite a decrease in surface area and pore volume there is an increase attributed to the strong affinity of the doped Li with H₂ gas molecules.

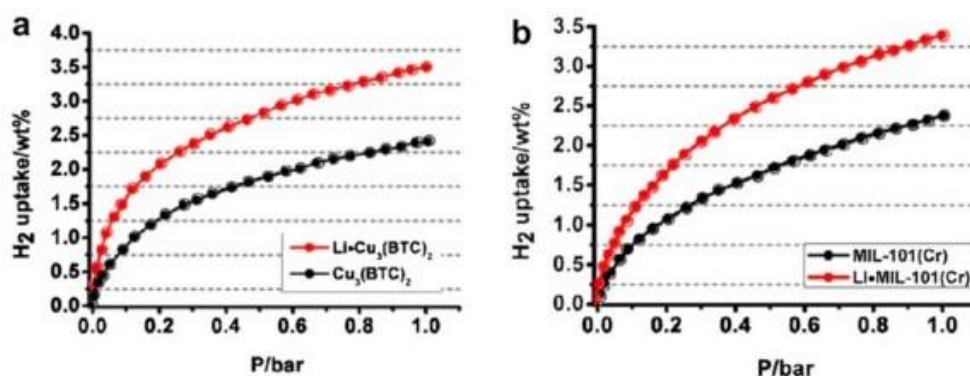


Fig. 1.10 H₂ adsorption isotherms at 77 K for **a)** Cu₃(BTC) and Li-Cu₃(BTC), **b)** MIL-101 and Li-MIL-101. Figures taken from reference 80.

1.1.6 MOFs Potential Use in Carbon Capture

There is a well-established link between increasing levels of CO₂ in the atmosphere with increasing global temperature and adverse weather effects, known collectively as climate change.^{81,82} Human activity has raised CO₂ concentration in the atmosphere; the industrial revolution initiated the burning of fossil fuels, releasing CO₂ as a by-product on a huge scale.⁸³ It is estimated that the average global temperatures will rise between 1.8 – 6.4 °C by the end of the 21st century.⁸⁴ There are several organisations around the world with the aim to reduce the world's carbon dioxide emissions – the international panel on climate change (IPCC), the department of energy and climate change (DECC) and the Kyoto protocol.^{85,86}

There is currently a vast amount of research into developing greener energy sources such as the use of biofuels which are compatible with many conventional engines and are blendable with fossil fuels.⁸⁷ As adaptation to low carbon and alternative energy technologies will require considerable research and development before implementation, methods for removing the CO₂ from emission streams was deemed paramount to avoid further exacerbating climate change.

Carbon capture is the process of removing CO₂ from flue gas.⁸⁸ There are currently technologies in place for removing CO₂; most commonly is the use of amine scrubbing which has been known since the 1930s, Fig 1.11.⁸⁹ The process involves absorbing CO₂ at near ambient temperature into a low volatility aqueous amine solution, typically monoethanolamine (MEA). The amine is then regenerated by stripping with water vapour, leaving pure CO₂ for sequestration. The energy cost of regenerating the amine is very high and therefore a more efficient process is sought. The ideal process should show a high affinity and selectivity towards CO₂ for efficient capture, however, the affinity should be sufficiently low to minimise the cost of regeneration of the material. One proposed solution is the physical adsorption of CO₂ into porous solid materials.

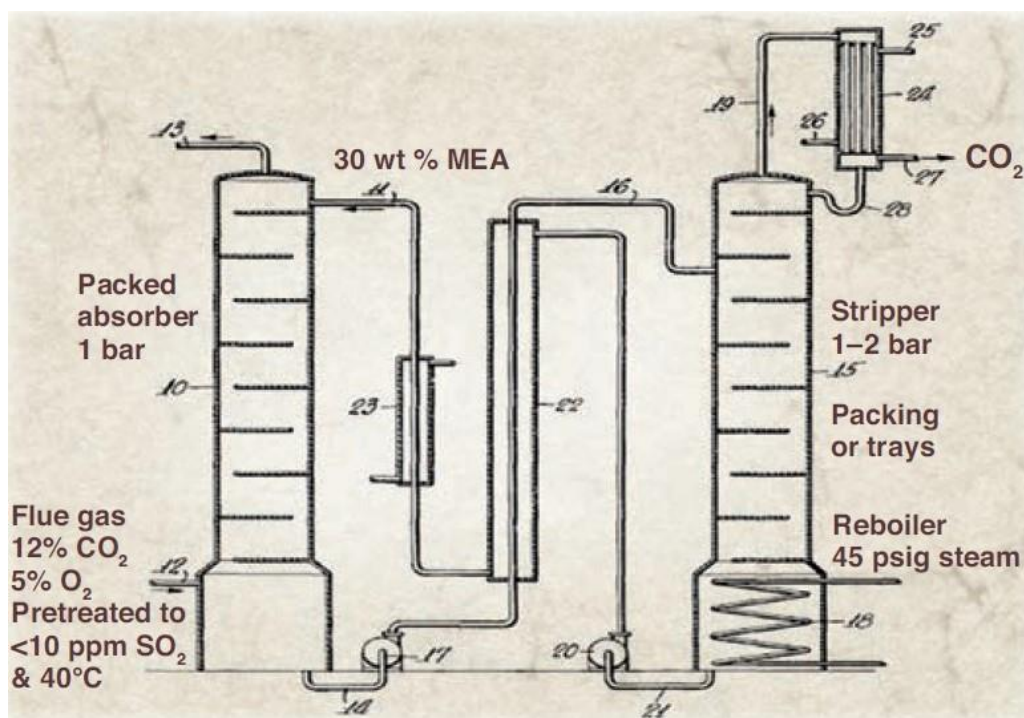


Fig. 1.11 Schematic of the amine scrubbing process for carbon capture. Figure taken from reference 89.

There are three types of CO₂ removal for potential carbon capture and sequestration processes: pre-combustion, post-combustion and oxy-fuel combustion (Fig. 1.12).⁹⁰ Oxy-fuel combustion relies on a supply of nearly pure oxygen for the combustion of fuels, which entails a high capital cost thus only pre-combustion and post-combustion separations will be discussed further.⁹¹ Pre-combustion separations involve the reaction of a primary fuel with air to produce H₂ and CO; further reaction of CO with steam produces CO₂. The CO₂ is then separated from the CO₂/H₂ mix and the H₂ is available for energy generation. Theoretically, this separation is easy to achieve, as MOFs have already shown greater affinity and uptake capacities for quadrupolar CO₂ vs. H₂. However, a high capital cost is required to construct suitable new power plants.^{92,93} Post-combustion separation is the most feasible route currently as construction of new plants would be avoided since necessary equipment can be

retroactively fitted to existing power plants that burn fossil fuels. This process involves the removal of CO_2 after the fuel has been burned, *i.e.* removal of CO_2 from flue gas. The key separation in post-combustion carbon capture is selection of CO_2 over N_2 , although other trace gases such as CO and H_2O are also present.⁹⁴

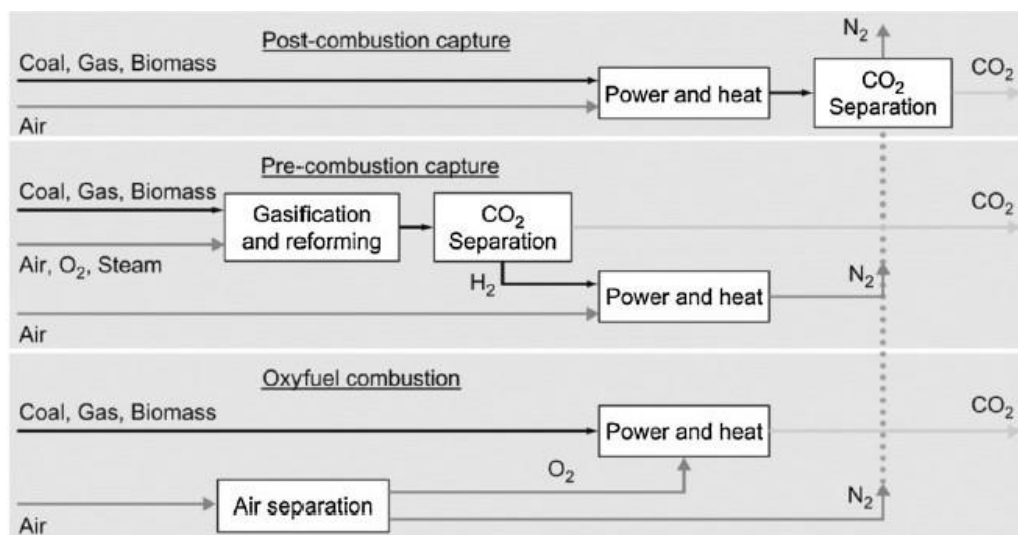


Fig. 1.12 The different carbon separation processes. Figure taken from reference 95.

MOFs have been proposed as a solution to this problem as they provide a potential for easy-on/easy-off selective adsorption for specific gases which require lower energy for regeneration.⁹⁶ The three different types of carbon capture require selective adsorption of CO_2 from different gas mixtures; post-combustion (CO_2/N_2 separation), pre-combustion (H_2/CO_2 separation) and oxy-fuel combustion ($\text{CO}_2/\text{H}_2\text{O}$ separation). Methods to increase the affinity of a framework for CO_2 include varying the metal centres and functionality in the organic ligand to optimise frameworks for use in carbon capture technologies.^{97,98} Zhang *et al.* reported the effects of temperature and linker functionality upon CO_2 capture.⁹⁹ At low pressures, up to 0.1 MPa, the CO_2 uptake is improved by the introduction of polar groups as the CO_2 molecules in the pores are not closely packed. Therefore the interaction between the

framework and the CO₂ molecules dominates uptake behaviour. The effect of the polar groups becomes less apparent on increasing temperature, reflected by the selectivities decreasing with increasing temperature. It was found that the linker functionality affected the separation of CO₂ from three different gaseous mixtures: CO₂/CH₄, CO₂/CO and CO₂/N₂.

Montoro *et al.* reported the effect of functionalisation of open metal sites with amines on the uptake of CO₂ with particular focus upon the effects of the amine stereochemistry on CO₂ capture.¹⁰⁰ HKUST-1 was functionalised with three different amines: ethylenediamine (HKUST1@en), 3-picolylamine (HKUST1@3pico) and 4-picolylamine (HKUST1@4pico). The PXRD patterns of the three functionalised materials show that the framework structure was preserved. Incomplete substitution of the open metal sites was achieved, likely due to steric hindrance within the pores. The N₂ adsorption uptake in the functionalised materials was lower than that observed for HKUST-1, possibly indicating that N₂ is no longer able to access the pores. There were no such problems observed for the CO₂ adsorption, at low pressures (<0.1 bar) HKUST1@3pico and HKUST1@4pico show a more rapid uptake than HKUST-1. This is indicative of the increased interactions between the framework and the CO₂. Detailed selectivity studies were carried out on HKUST1@3pico and compared with HKUST-1 by variable temperature pulse gas chromatographic experiments in the temperature range 313 - 333 K and using an equimolar gas mixture of N₂, CO₂ and H₂. Both materials exhibited a large retention time for CO₂, although the retention time is longer in HKUST1@3pico indicating. Both H₂ and N₂ show weaker interactions. HKUST1@3pico also shows a higher heat of adsorption than HKUST-1, the

values being 28.2 kJ mol^{-1} and 21.4 kJ mol^{-1} respectively. The difference in the heat of adsorption can be explained by the interaction of CO_2 with the basic amine sites and the adjacent Cu open metal sites.

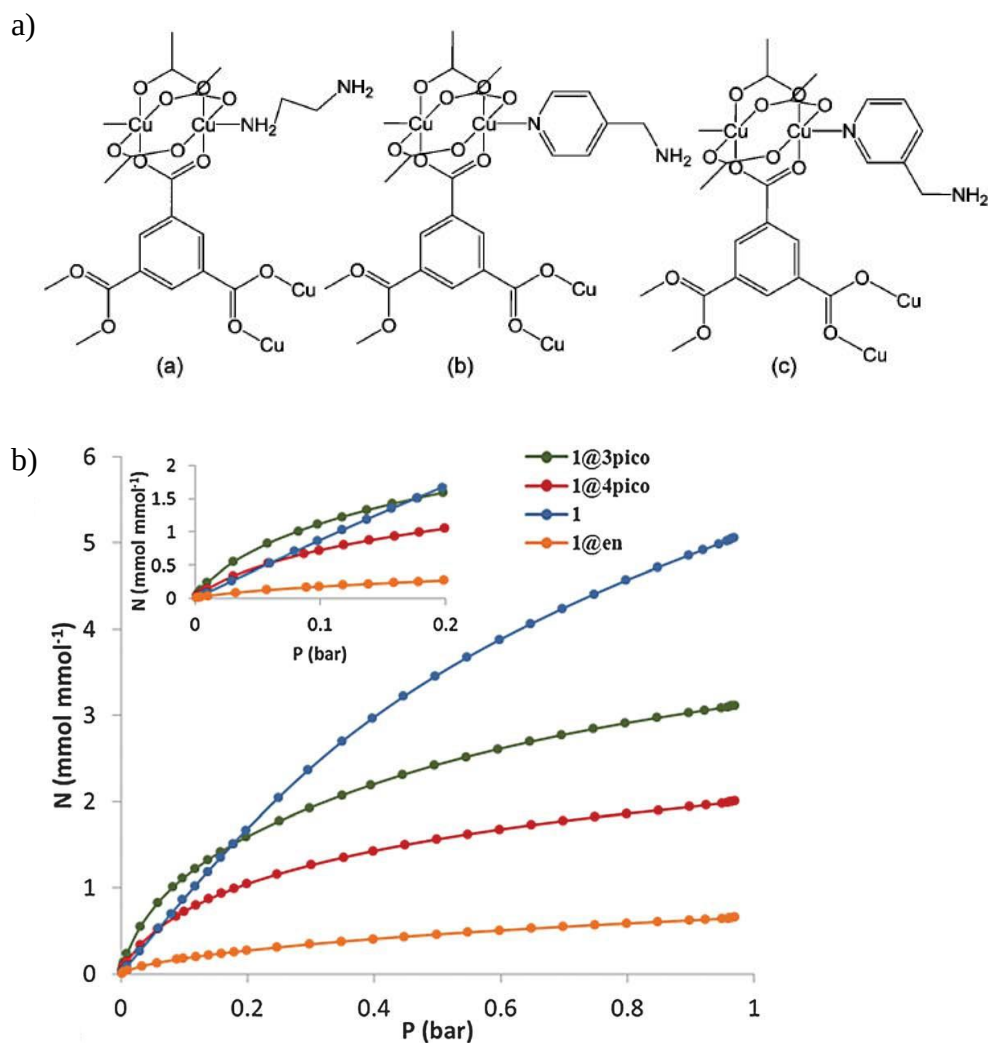


Fig. 1.13 a) The functionalisation of the Cu-paddlewheel unit with three different amines, **b)** The CO_2 adsorption isotherm at 273 K showing the increased adsorption of the amine functionalised material at low pressures. Figures taken from reference 100.

1.1.7 MOFs Used in Hydrocarbon Separations

Crude oil consists primarily of hydrocarbons with varying chain lengths, along with other organic compounds.¹⁰¹ The hydrocarbons are separated into commercial products by fractional distillation, Fig 1.14. Hydrocarbons with

longer C-chains, 7 or more, are used in fuels such as diesel, gasoline and jet fuel. The smaller hydrocarbons have more varied applications, such as aerosols (butane), cooking (propane) and feedstock for plastic production (ethylene).¹⁰² The separation of hydrocarbon mixtures from the same fraction is much more difficult, as the mixtures tend to contain alkanes, alkenes and alkynes with similar C chain lengths, boiling points and sizes.^{103,104} C₂ hydrocarbons are mixed with methane and their separation is important for the use of CH₄ as a fuel.¹⁰⁵

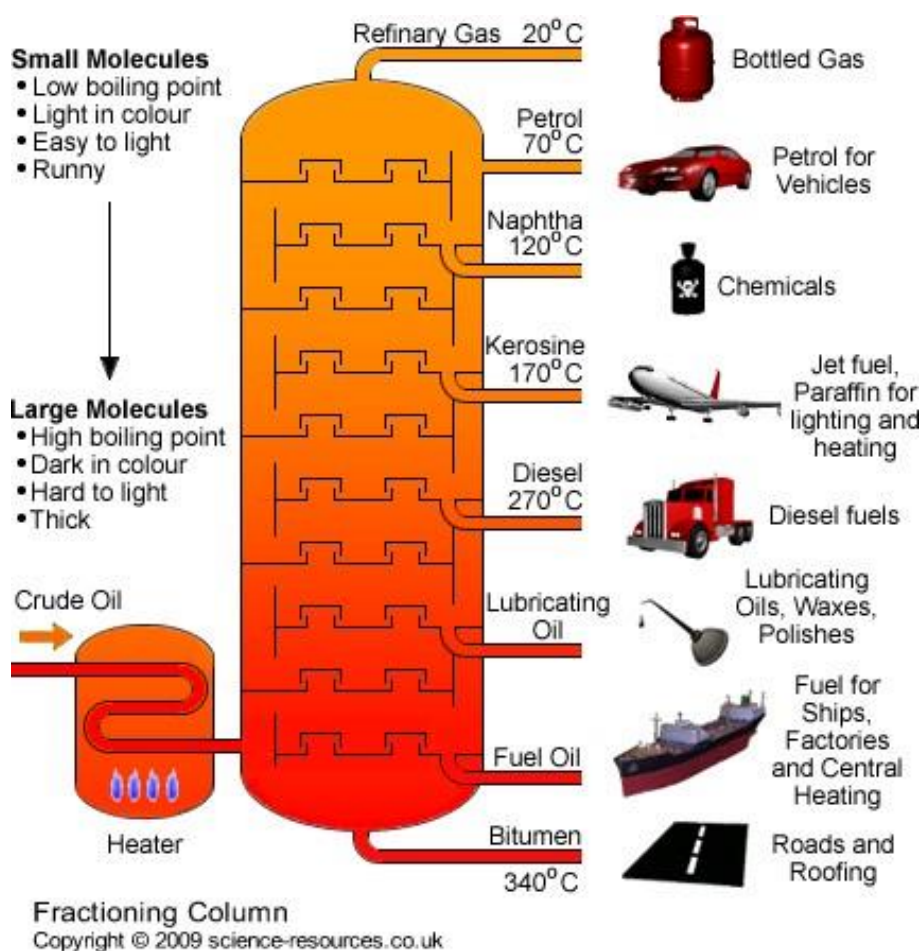


Fig. 1.14 Schematic of the fractional distillation of crude oil. Figure taken from reference 106.

The industrial uses for each of the C₂ hydrocarbons, requires pure feeds of the desired hydrocarbon. Acetylene has uses in welding work, oxy-acetylene torches are used for both welding and cutting of metals. Ethane is used as a refrigerant in cryogenic refrigeration systems. Both ethane and acetylene are precursors for the generation of ethylene.¹⁰⁷ Ethylene is one of the most widely used small hydrocarbons in industry and nearly 25 trillion tons is generated per year.¹⁰³ It is most commonly used as a feedstock for polymer and plastic synthesis. The C₂ hydrocarbons are also found as contaminants in natural gas, therefore the separation of C₂ hydrocarbons from natural gas is crucial.

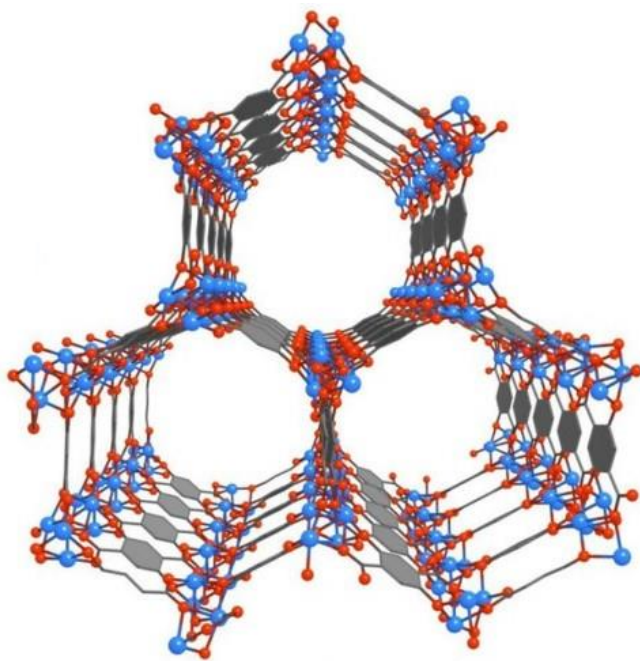
Currently the separations of C₂/CH₄ and alkene/alkane (C₂H₄/C₂H₆) mixtures are performed using cryogenic distillation which requires low temperatures and high pressures.¹⁰⁸ These separation processes are among the most expensive and energy intensive large scale separations carried out in the chemical industry. Therefore, substantial research is conducted investigating alternatives for the separation of C₂ and C₂/CH₄ hydrocarbons, such as selective adsorption on solid supports.

MOFs have been proposed for the efficient and low energy process of the separation of hydrocarbon mixtures. The tunability of the framework structure makes these materials attractive candidates for this process. The separation of alkene/alkane (C₂H₄/C₂H₆) mixtures in MOFs can be achieved *via* two methods, the first being through size selective adsorption and the second utilising a difference in strength of interaction with the framework.¹⁰³

One framework that utilises the differences in strength between the adsorbed gas and the framework structure is MOF-74. Fe-MOF-74 [Fe₂(dobdc)]

(dobdc - 4,6-dioxido-1,3-benzenedicarboxylate) is a 3D framework with channels with a diameter of 11 Å lined with square-pyramidal Fe(II) cations.¹⁰⁹ After activation, each Fe(II) cation is left with an open coordination site that is accessible to incoming adsorbate gas molecules. There is a high surface density of available Fe sites within the framework, with small spacings between Fe atoms (6.8 and 9.0 Å).

a)



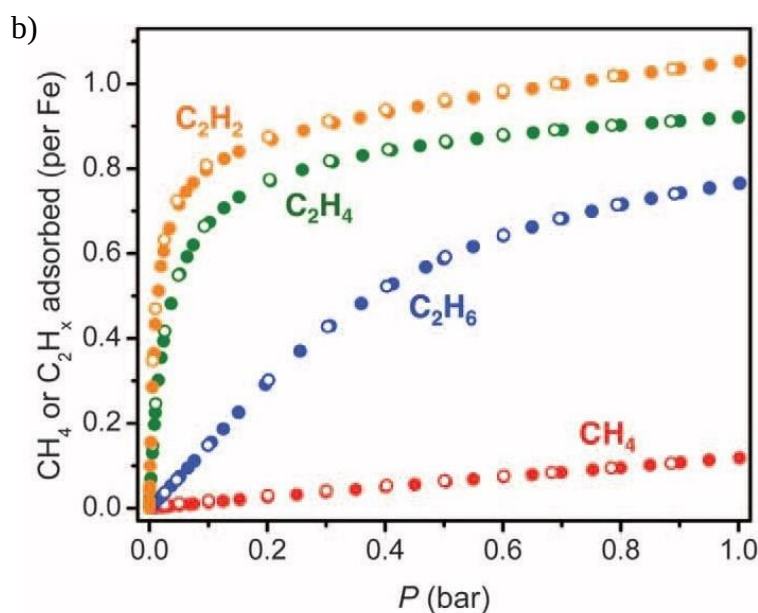
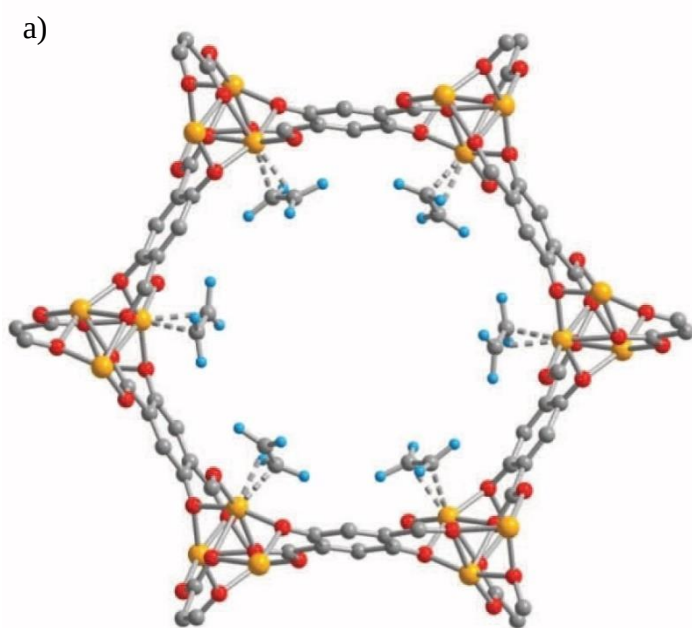


Fig. 1.15 a) Crystal structure of Fe-MOF-74 showing the porous nature of the material. **b)** Hydrocarbon adsorption isotherms for Fe-MOF-74. Figures taken from reference 109.

Single component adsorption isotherms were measured for CH₄, C₂H₂, C₂H₄ and C₂H₆ at 318, 333 and 353 K, whilst the data collected at 313 K was used for the selectivity calculations. The material displayed much stronger affinity for the unsaturated hydrocarbons (C₂H₂ and C₂H₄); this can be seen in the adsorption isotherms as there is a steep rise in uptake at low pressures (Fig.1.15). The uptake capacity for C₂H₆ is lower than that observed for the saturated hydrocarbons, but is higher than that recorded for CH₄ as CH₄ has a lower polarisability compared with C₂H₆. Gas loaded *in situ* neutron diffraction studies of the MOF were carried out in order to probe the dynamics of the substrate binding with the open Fe(II) sites. Reitveld refinement of the data indicated only one adsorption site located within the framework corresponding to the open coordination site at Fe. Both C₂H₂ and C₂H₄ bind in a side on fashion with distances ranging from 2.4 - 2.5 Å. The interaction between the Fe cation and C₂H₆ is much weaker as can be seen by the longer distance of ~ 3 Å. The differences in the strengths of

interaction can also be supported by the calculated heats of adsorption for each gas within the framework. Both C_2H_2 and C_2H_4 display a much higher heat of adsorption (47 and 45 kJ mol^{-1} respectively) compared with C_2H_6 (25 kJ mol^{-1}). The heat of adsorption for C_2H_2 and C_2H_4 decrease significantly as the loading approaches one gas molecule per Fe cation, consistent with the exposed cation sites being the strongest adsorption sites within the structure. The calculated IAST selectivity for $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ separations is in the range of 13 – 18, depending on the pressure. This is one of the highest reported $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ selectivities for a MOF material and is achieved through exploitation of the differences in strength of interaction between C_2H_4 and C_2H_6 with the open Fe sites. However, Fe-MOF-74 appears to show little to no selectivity for $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ as shown by the similar uptake capacities and similar heats of adsorption.



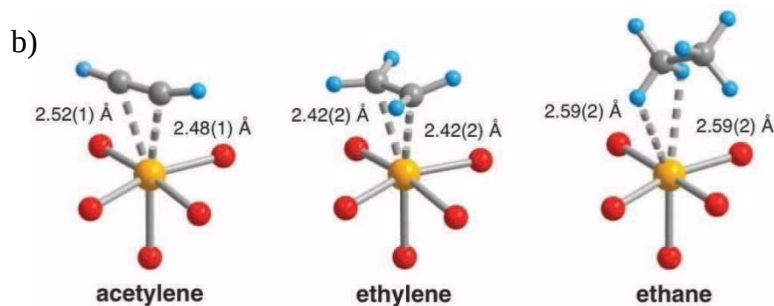


Fig. 1.16 a) Visualisation of C₂D₄ in the channels of Fe-MOF-74 showing the main interactive site at the open Fe centres, **b)** Visualisation of the interaction between the open Fe sites and the adsorbed hydrocarbons. Figures taken from reference 109.

A breakthrough experiment was performed on an equimolar mix of C₂H₄/C₂H₆ at 318 K resulting in separation of the components to 99.0 and 99.5 % purity, respectively (Fig. 1.17). Fe-MOF-74 also displays exceptional C₂/C₁ selectivity calculated using IAST, C₂H₂/CH₄ - 700, C₂H₄/CH₄ - 300 and C₂H₆/CH₄ - 20. All the C₂ hydrocarbons are able to bind more strongly with the open Fe(II) site.

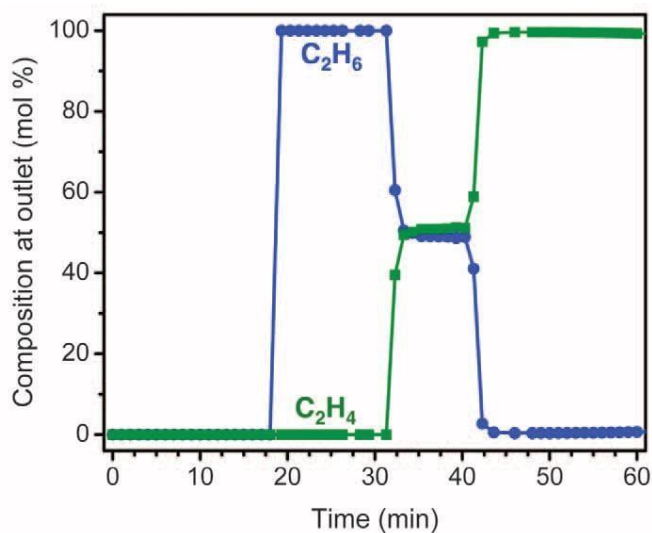


Fig. 1.17 Breakthrough curve showing the separation of C₂H₄ and C₂H₆ in Fe-MOF-74. Figure taken from reference 109.

A similar study on Mg-MOF-74 found that the harder coordinative nature of Mg compared to Fe leads to a decrease in gas adsorption capacity and a decrease in C₂H₄/C₂H₆ selectivity owing to the decreased amount of backbonding.¹⁰⁴

Amongst other MOF-74 analogues it was found the C_2H_4/C_2H_6 selectivity in the dobdc materials follows the trend $Fe > Mn > Ni \approx Co > Mg > Zn$, likely associated with the relative softness of the metal centre.¹⁰²

1.2 Aims and Objectives

There has been extensive research into how changes in ligand structure, shape and functionality affect the gas adsorption properties of a MOF, *i.e.* the uptake capacity or selective adsorption for a particular gas. There have been some examples on how the change in metal ion affects these same properties such as the MOF-74 series and MIL-53 series previously discussed, however, examples of these kinds of study are rare. Therefore, this thesis focuses on how changing the metal ion affects the adsorption behaviour in a series of analogous MOFs, focussing particularly on CO_2 and C_2 hydrocarbon adsorption and selectivity.

Chapter 2 focuses on the synthesis of NOTT-300(Cr) and how the CO_2 adsorption differs to that reported for NOTT-300(Al). The selective adsorption of CO_2 over CH_4 and N_2 for the two materials is investigated *via* various methods. The change in metal centre is thought to change the adsorption properties through its effect on the bridging -OH group which plays a key role in interactions with adsorbed guest species.

The aim of Chapter 3 is to investigate this concept further by synthesising a series of mixed metal NOTT-300(AlCr) frameworks to study how the variation in the ratio of cation content affects the CO_2 adsorption and selectivity.

The focus of Chapter 4 is on the C_2 hydrocarbon adsorption in this same series of MOFs, NOTT-300(Cr) and the NOTT-300(AlCr) series. The adsorption

capacities for each C₂ hydrocarbon and the potential to separate C₂ hydrocarbon mixtures and C₂/C₁ hydrocarbon mixtures is studied for all the materials to see how the ratio of the cation content affects the adsorption of these gases.

1.3 Experimental and Theoretical Techniques Used

1.3.1 Synchrotron Powder X-ray Diffraction (PXRD)

Diffraction is the scattering phenomenon that occurs when an X-ray beam interacts with a crystalline, ordered structure. At certain “in phase” directions within a crystal the diffracted beam is more intense; these directions can be expressed in the form of Bragg’s Law (equation 1.1).

$$n\lambda = 2d\sin\theta \quad (1.1)$$

Where n is the order of diffraction, d is the spacing between diffraction planes in the crystal and λ is the wavelength of the radiation used.

MOFs are not always afforded as large enough single crystals for single crystal diffraction to be used and therefore must be analysed by powder X-ray diffraction (PXRD). A powder sample consists of a collection of very small crystallites, with sufficient crystallites in the correct orientation for Bragg’s Law to be satisfied and for diffraction to occur. In some cases the sample can align along a specific plane, known as preferred orientation, which can result in the omission of peaks in the diffractogram and can also affect the peak intensity displayed. This is minimised by grinding the sample prior to the experiment and/or by spinning the sample during data collection.

During a PXRD experiment a sample is loaded on to a disc or into a capillary and placed in the path of an X-ray beam. The X-rays are diffracted by ordered atoms in the sample and then hit the detectors which scan 2θ , and the results are recorded as a diffractogram (Fig. 1.18). Structure refinement from PXRD data is much more difficult compared with single crystal, as the three dimensions of the crystallographic data has been condensed into two dimensions of the diffractogram.

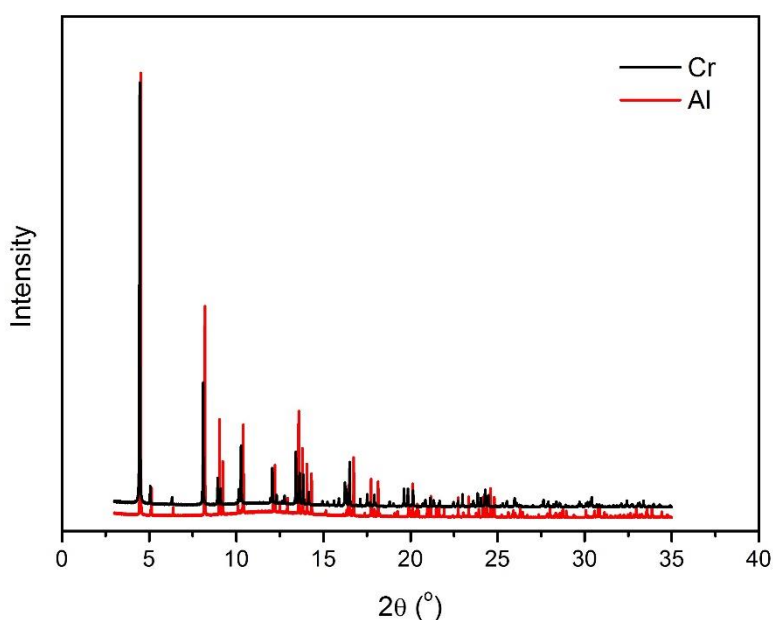


Fig. 1.18 Example of a diffractogram obtained from powder X-ray diffraction.

A significant number of the PXRD experiments carried out for this thesis were conducted at beamline I11 at Diamond Light Source (DLS), a synchrotron facility. A synchrotron works by first producing electrons from an electron gun which are accelerated to very high speeds using three different accelerators – the linear accelerator, the booster synchrotron and the large storage ring. The storage ring is not a true ring and is actually a polygon, at DLS it is a

tetracontakaioctagon shape made up of 48 straight sections angled together with 48 bending magnets. The bending magnets control the path of the electrons around the ring. Bending of the path of electrons results in energy lost in the form of light which is filtered and focussed by a series of monochromators, slits and mirrors before being used on the different beamlines.

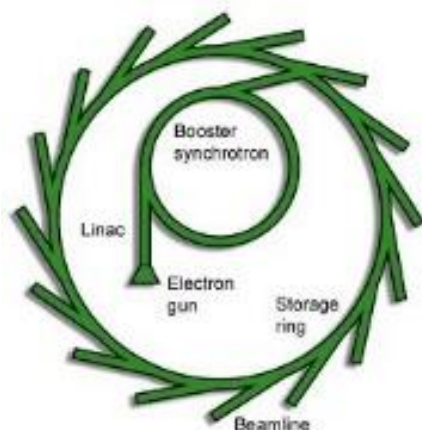


Fig. 1.19 Representation of a synchrotron facility. Figure taken from reference 110.

Synchrotron PXRD offers some advantages over typical lab-scale X-ray diffractometers. The intensity of the X-ray beam is much higher, allowing for quicker collection times and high angular resolution is also possible. Lab-scale diffractometers often use Cu as the source of X-rays. This can be problematic for MOF samples containing Co as they fluoresce at this wavelength; another advantage for using synchrotron radiation is that this does not occur as the radiation wavelength is different.

1.3.2 Inelastic Neutron Spectroscopy (INS)

Neutrons are large elementary particles with zero charge resulting in them being highly penetrating making it possible to assess a bulk sample effectively (as in not just the surface). When compared with electromagnetic radiation they

interact very differently. Scattering occurs when the neutrons collide with the nucleus of the atom rather than being scattered by electron shells like photons do. This results in a highly unpredictable scattering cross section for all elements and their scattering cross sections have all been determined experimentally.

There are several advantages for using neutron spectroscopy such as the absence of selection rules for observable transitions thus all vibrations are active and measurable, in principle. The observations are not restricted to the Brillouin zone (gamma point) as is the case for optical techniques. The wavelength is easily varied to match the atomic spacings in the sample. The intensity of a scattered signal can be predicted for a given molecular model as the intensities are proportional to the concentrations of elements within the sample and their cross sections thus the measured intensity are straightforwardly relatable to the associated displacements of the scattering atom.

The scattering of a neutron by a sample is characterised by the change in its momentum (P) and energy (E), the momentum and energy gained by the scattered particle is the equal to that lost by the sample and *vice versa* (Fig. 1.20). The momentum transfer and energy transfer are defined in equation 1.2.

$$\begin{aligned} P &= \hbar k_i - \hbar k_f = \hbar Q \\ E &= \hbar \omega_i - \hbar \omega_f = \hbar \omega \end{aligned} \quad (1.2)$$

Where k is the wave vector, ω is the angular frequency and Q is the scattering vector. The intensity of a scattered signal is given in terms of the scattered vector and angular frequency, S (Q, ω). There are two types of scattering: elastic, where

there is no energy transfer between the neutron and the sample, and inelastic, where the neutron either gains or loses energy after collision with the sample.

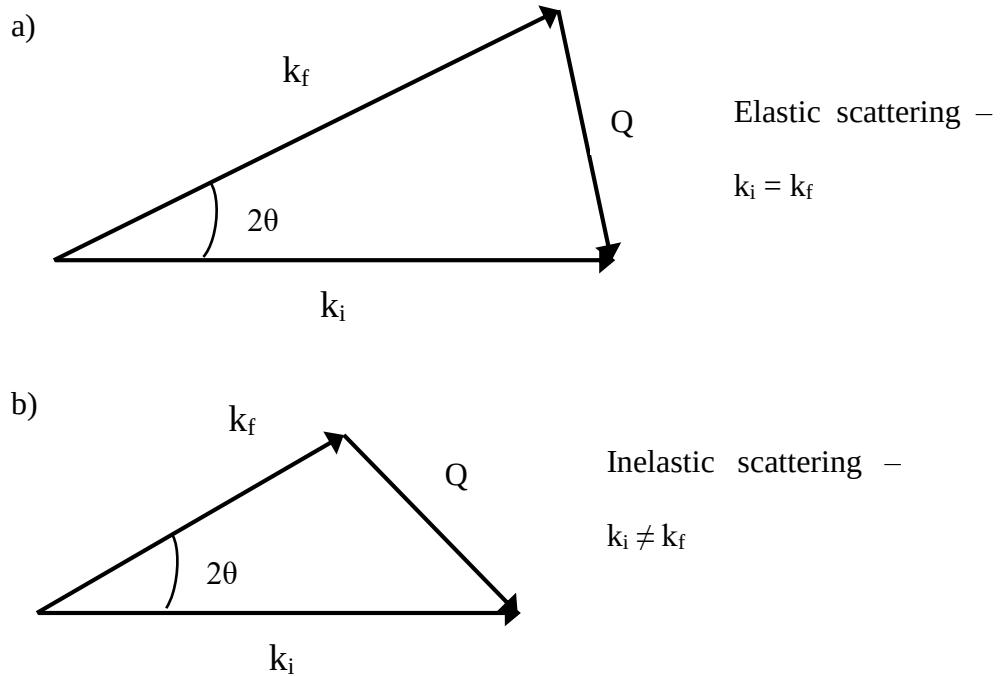


Fig. 1.20 Scattering triangles for **a)** elastic scattering and **b)** inelastic scattering. In both scattering events the neutron is scattered through the angle 2θ and the scattering vector is given by the relationship $Q = k_i - k_f$.

1.3.3 Dual-Component Adsorption and Breakthrough Experiments

In a typical gravimetric gas adsorption experiment (Fig. 1.21), as presented in this thesis the MOF sample is loaded into a suspended glass crucible inside a reactor chamber. A pure gas is flowed into the chamber until the set pressure point is reached and the system allowed to equilibrate before change in weight is recorded. The flow of gas is controlled by a mass flow controller (MFC), allowing for better precision at low pressures (by using slow flow rates) and quick pressure ramping times at high pressures (by using fast flow rates). This process continues until the desired pressure range has been covered (*e.g.* 0 – 20

bar in 500 mbar steps), the exhaust valve remains closed during this entire process to maintain the pressure. After the desired final pressure is reached and the data point recorded, the sample chamber is slowly opened to the exhaust/vacuum pump in stages so the desorption isotherm can be likewise recorded at different pressure intervals.

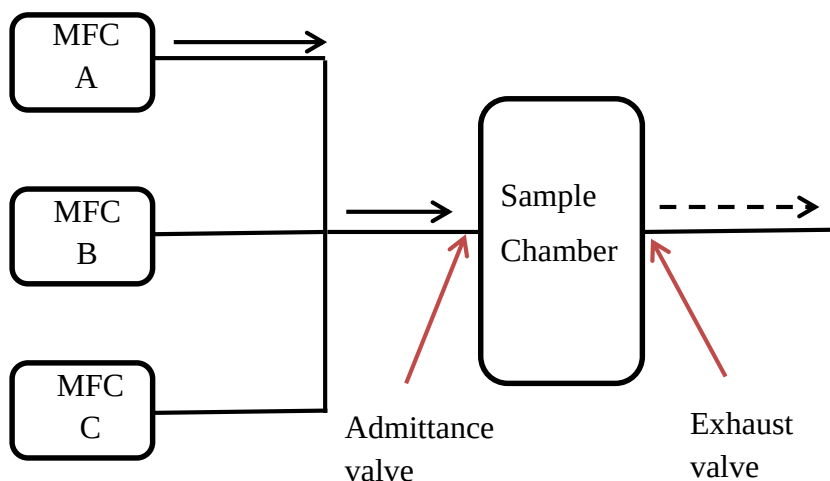


Fig. 1.21 Schematic of a static gravimetric adsorption experiment, where the inlet of gas is controlled by the admittance valve and the exhaust valve remains closed until desorption.

In contrast, during a flow (single component) gas adsorption experiment or a dual-component adsorption experiments the admittance valve and exhaust valve remain open throughout the entire adsorption and desorption that is recorded. This allows the sample to be in a constant environment of the desired mixture of gases which is constantly refreshed (Fig. 1.22). This type of experiment can be used to investigate whether a material shows an increased selectivity for one gas over another (*e.g.* CO₂ vs. N₂), especially when used along with selectivity calculations such as IAST selectivity.

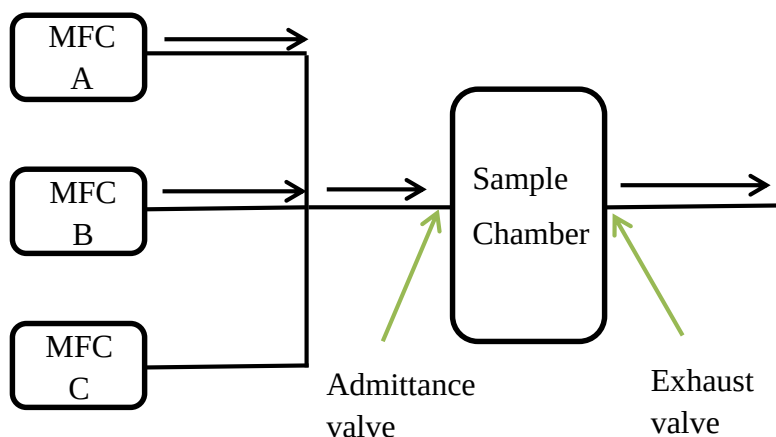


Fig. 1.22 Schematic of a flow gravimetric adsorption experiment, where a constant flow of gas is controlled by the MFCs and both the admittance and exhaust valve stay open throughout the experiment.

There are several different types of isotherm shape observed in adsorption (I - V), depending on the process occurring during adsorption. Most commonly seen in this thesis is a Type-I isotherm, indicative of monolayer adsorption. This is also known as Langmuir adsorption. Also seen, in N₂ adsorption at 77 K mainly, is a Type-II isotherm. Type-II isotherms do not exhibit a saturation level, as seen by the plateau in Type-I isotherms. This indicates the start of multi-level adsorption after the formation of the monolayer. Examples of both of these can be seen in Fig. 1.23.¹¹¹

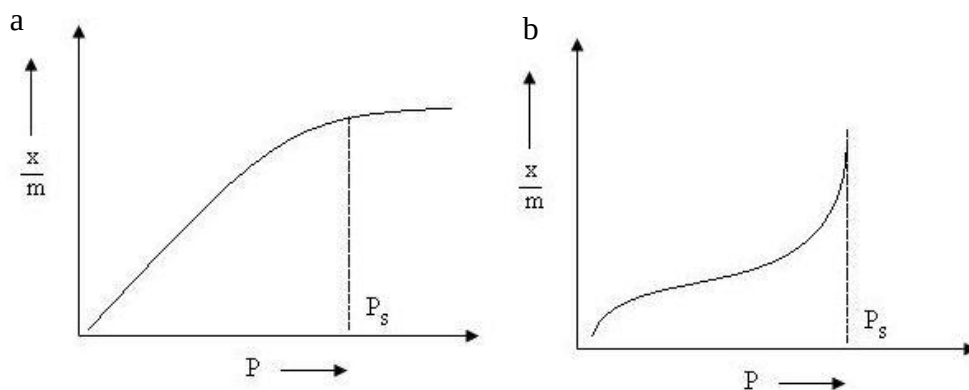


Fig. 1.23 The different types of adsorption isotherm found in this thesis showing **a)** Type-I adsorption and **b)** Type-II adsorption.

Breakthrough experiments are performed in an automated breakthrough reactor (ABR), which is a separate part of the IGA instrument. The gas flow is controlled by the same MFCs, however, the sample is now packed into a fixed bed and the exiting gas stream is analysed by mass spectrometry (Fig. 1.24). A mixture of gases is flowed over the fixed bed of sample and the time taken for the gas to travel through the sample and be detected is recorded. This is known as the breakthrough time and is a measure of the separation ability of a material.

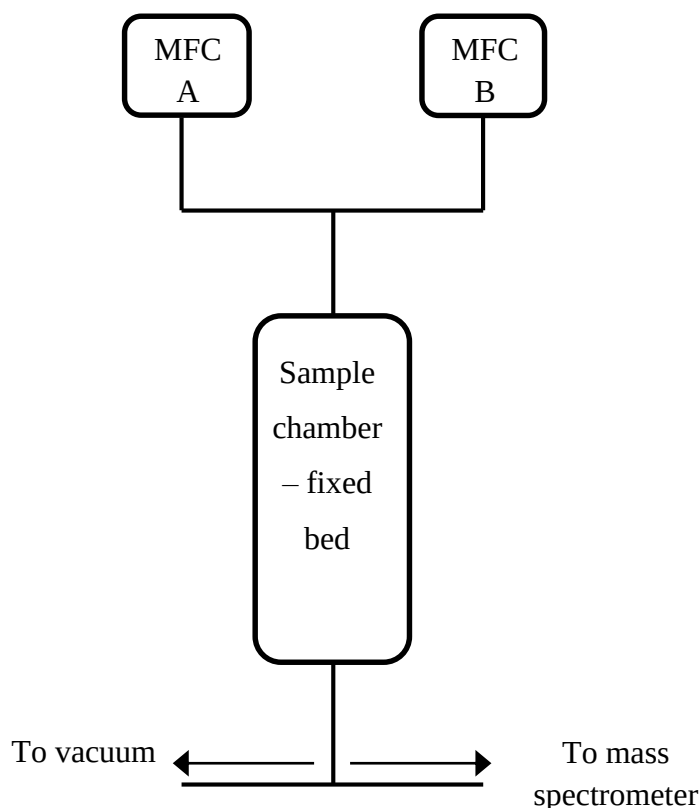


Fig. 1.24 Schematic of a breakthrough adsorption experiment performed in an ABR.

1.3.4 Ideal Adsorbed Solution Theory (IAST)

The ideal adsorbed solution theory (IAST) is used throughout this thesis for selectivity calculations and gas uptake predictions.^{112,113} The IAST model allows for calculation of the selectivity of a binary gas mixture based on the single component adsorption data. The number given is an indication of preferential adsorption, the higher the number the higher the selectivity for that species *i.e.* a CO₂/N₂ IAST selectivity of 80 means the material is 80 times more likely to adsorb CO₂ than N₂. To do this the following experimental data are required – the composition of the adsorbed phase (x_i), the composition of the gas phase (y_i), the total pressure, the spreading pressure (π) and the pure component adsorption data for each adsorbate used. The spreading pressure can be defined as:

$$\pi(P_i^0) = \frac{RT}{A} \int_{t=0}^{P_i^0} n_i^0(t) d \ln t \quad (1.3)$$

Two relationships can be yielded from equation 1.3, the spreading pressure of each component can be written as a function of pressure.

$$\begin{aligned} \pi_1^0 &= \psi_1(P_1^0) \\ \pi_2^0 &= \psi_2(P_2^0) \end{aligned} \quad (1.4)$$

Assuming the mixture of gases is an ideal solution, this means that the interaction between the different components does not differ from interactions between the individual components, the equilibrium pressure for the mixed gas adsorption can be related to the equilibrium pressure of the pure component and the mole fraction of the adsorbed gas, equation 1.5.

$$\begin{aligned} P_{y1} &= P_1^0 x_1 \\ P_{y2} &= P_2^0 x_2 \end{aligned} \quad (1.5)$$

In a binary mixed system, the total pressure can be expressed as a sum of the equilibrium pressures of the mixed gas system.

$$P = P_{y1} + P_{y2} = P_1^0 x_1 + P_2^0 x_2 \quad (1.6)$$

The mixing process is stated to occur at constant spreading pressure (π) and thus the spreading pressure of each component is the same.

$$\pi_1^0 = \pi_2^0 \quad (1.7)$$

It can be said that in a binary mixed gas system, the total composition of the gas phase and the adsorbed phase are equal to 1.

$$\begin{aligned}x_1 + x_2 &= 1 \\y_1 + y_2 &= 1\end{aligned}\tag{1.8}$$

This gives a total of seven independent equations with nine unknown variables, making it impossible to solve the equations. Therefore it is necessary to eliminate some of the unknown variables in order to calculate the selectivity. The total pressure in the mixed gas system can be specified as 1 bar and therefore from this it can be deduced that in an equimolar system $y_1 = y_2 = 0.5$. Equation 1.3 can now be simplified to equation 1.9.

$$\frac{\pi A}{RT} = \int_{t=0}^{P_i^0} n_i^0(t) \frac{1}{t} dt\tag{1.9}$$

The adsorption of component i can be written as a function of the equilibrium pressure as shown in equation 1.10.

$$n_i^0 = F_i(P_i)\tag{1.10}$$

This new variable, F , can be calculated using the Langmuir-Freundlich model to fit the single component adsorption isotherms. The Langmuir-Freundlich model relates the adsorbed amount (Q), with the saturated amount ($Q_{\max}$), the Langmuir coefficient (B) and the pressure (P).

$$F = Q = \frac{Q_{\max} B P^v}{1 + B P^v}\tag{1.11}$$

As the spreading pressure of each of the components is the same, equation 1.9 can now be written giving π as a function of F .

$$\int_{t=0}^{x_1} \frac{P y_1}{F_1(t)} d \ln t = \int_{t=0}^{x_2} \frac{P y_2}{F_2(t)} d \ln t \quad (1.12)$$

Once all the unknown variables are found, the selectivity (S) is calculated using equation 1.13.

$$S = \frac{x_1/y_1}{x_2/y_2} \quad (1.13)$$

The IAST model can be used further, not just for selectivity calculations, for the prediction of gas uptake in a binary mixed system ($x_{1,2}$). This is done using the mole fraction of each adsorbed gas (x_i) and the adsorbed amount at the equilibrium pressure (n_i), equation 1.14. The value obtained is in mmol g^{-1} and simply needs converting to wt% so it can be compared to the experimental gas uptakes of a binary mixed system which are reported in wt%.

$$x_{1,2} = \frac{1}{(x_1/n_1 + x_2/n_2)} \quad (1.14)$$

1.4 References

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Chapter 2 – Synthesis and Gas Adsorption Properties of NOTT-300(Cr)

2.1 Introduction

2.1.1 M(III)-based MOFs for CO₂ separation

As discussed in Chapter 1 MOFs can show excellent potential for application in CO₂ separation owing to their large internal surface area and possible favourable guest-host interactions. There is an abundance of literature reporting the synthesis, structure and properties of MOFs with a rapid increase in number of publications over the past decade.¹ A large number of the published MOFs are constructed from M(II) metal centres/ions^{2,3,4} predominantly Cu(II) (*e.g.* HKUST-1)⁵ and Zn(II) (*e.g.* MOF-5).⁶ Examples of M(III) MOFs, although fewer, have been increasing in number over recent years with Al(III), In(III) and Cr(III) being the most common choice of metal ion.^{7,8,9} There are fewer examples of Sc(III)¹⁰ and Ga(III)¹¹ MOFs in the literature. One reason for the low number of M(III) MOFs in literature is that they tend to form microcrystalline products leading to difficulties in structure determination.¹² Structures are much more difficult to determine from powder X-ray diffraction compared to single crystal diffraction and so these materials are often not investigated fully. Even with these drawbacks, there are many reasons to proceed with the synthesis of M(III) MOFs such as environmentally benign nature¹³ and relative low cost¹⁴ making them attractive for industrial applications. Both Al(III) and Cr(III) MOFs tend to display high thermal stability and good uptake capacity for CO₂.^{15,16,17} Al-MOFs can also be synthesised in water, a green solvent, compared to many M(II) MOFs which are synthesised in highly toxic dimethylformamide (DMF) and other organic solvents.^{18,19} Many M(II) MOFs also exhibit poor stability to water vapour, decomposing upon introduction in the environment, making them unviable for many industrial applications in

which water vapour is present such as CO₂ capture from flue gas. Stability to water is a key property that makes studying M(III)-based MOFs of great interest.

One of the most extensively studied Al(III) MOFs in the literature is MIL-53(Al).²⁰⁻²⁶ The reasons for this are due to the ease of its synthesis, the availability of starting materials and the high stability of the framework. The structure consists of infinite chains of corner sharing [AlO₆] octahedra linked by 1,4-benzenedicarboxylate. These Al(III) octahedra are joined through *trans*-μ₂-OH groups. MIL-53(Al) also exhibits interesting properties such as a “breathing” mechanism upon adsorption and desorption of certain species, such as CO₂. This breathing phenomenon leads to a possibility for high CO₂ selectivity as breathing is not observed in the adsorption of gases such as N₂ and CO that do not directly interact with the framework. There is a clear step displayed in the CO₂ adsorption isotherm, indicating the opening of the framework and increased capacity for CO₂ at these increased pressures. MIL-53(Al) reaches an uptake of 9.9 mmol g⁻¹ at 294 K and 20 bar. At lower pressures, however, the uptake is quite low at only 2.7 mmol g⁻¹ at 1 bar. There have been several reports on the functionalization of MIL-53(Al) with groups such as amines,²³ in an effort to increase the number and strength of the interactions between the framework and adsorbate molecules. The “breathing” transition in MIL-53(Al) has also been studied and confirmed by various PXRD studies.^{24,25}

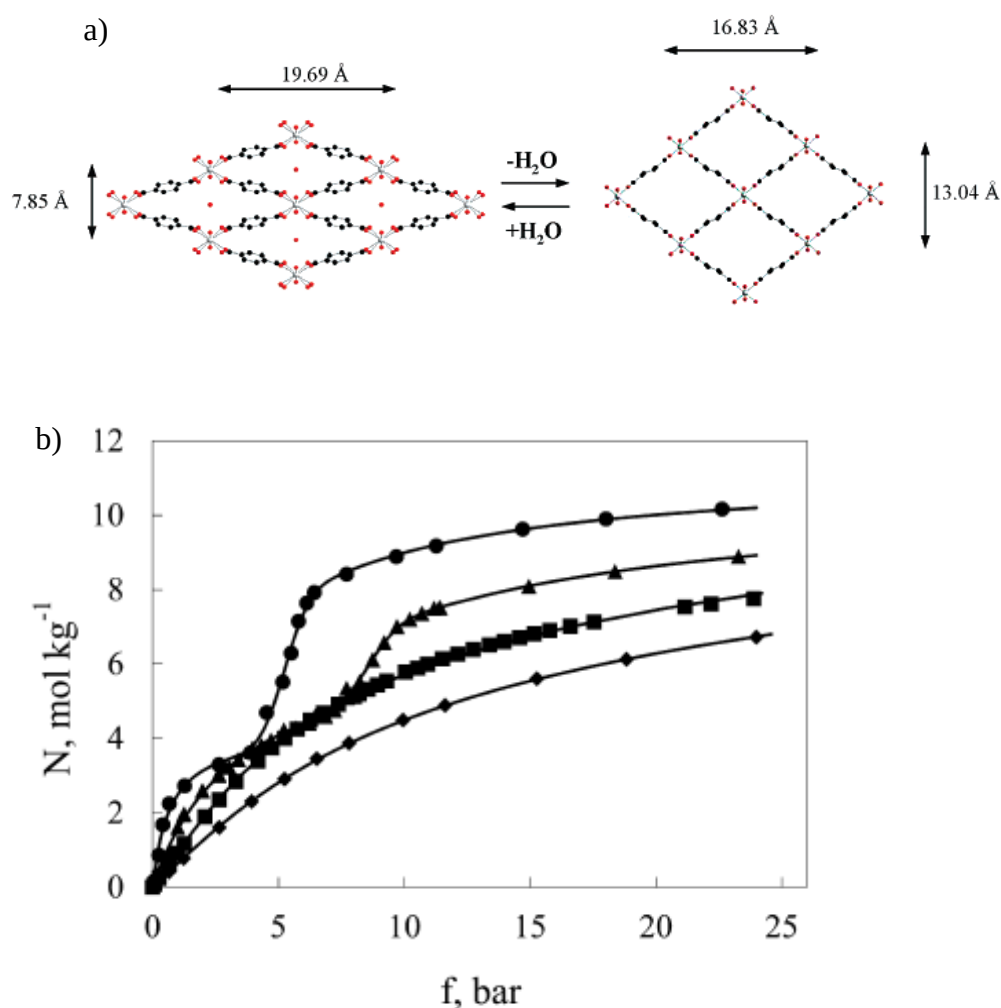


Fig. 2.1 a) Structure of MIL-53 in both unactivated (closed) and activated (open) forms to show the “breathing” of the framework. Figure taken from reference 22 **b)** CO₂ adsorption isotherms for MIL-53 (circles – 284 K, triangles – 314 K, squares – 332 K, diamonds – 350 K). Figure taken from reference 21.

A series of analogues of MIL-53 based upon Cr, Sc, Ga and Fe has been reported by Ferey *et al.*²⁷⁻³⁰ MIL-53(Cr) exhibits the same breathing phenomenon upon desolvation/solvation of the framework. The removal of guest solvent molecules from the pore results in a “closed pore” (cp) structure with the overall porosity reducing by ~30 %. The cp phase of this material is stabilised by H-bonds between the framework struts, and thus the “open pore” phase can only be

achieved by the adsorbate breaking these H-bonds and opening the structure, allowing further adsorption of substrates. In MIL-53(Cr) one adsorbate capable of breaking these H-bonds is CO₂, and with most other gases no phase change is observed. This could potentially give a high selectivity for CO₂; however, this opening behaviour is only observed at increased pressure (~6-8 bar). At lower pressures, where it is relevant for industrial separations, the uptake of CO₂ is unremarkable, < 3 mmol g⁻¹, similar to uptakes recorded for MIL-53(Al).

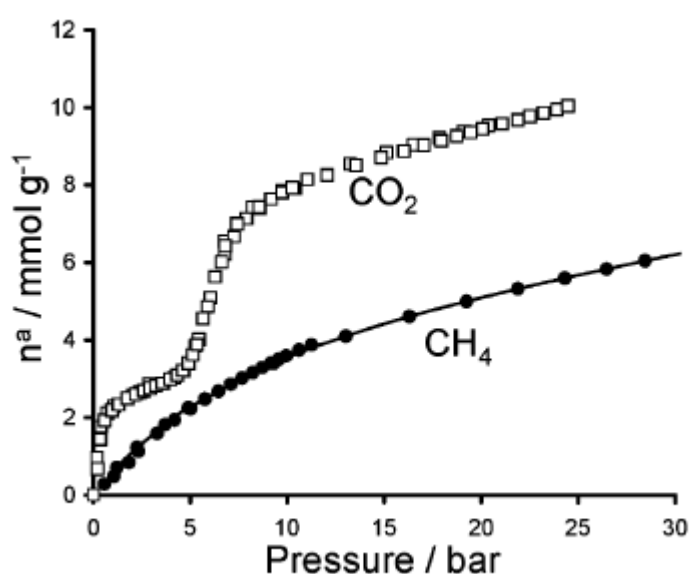
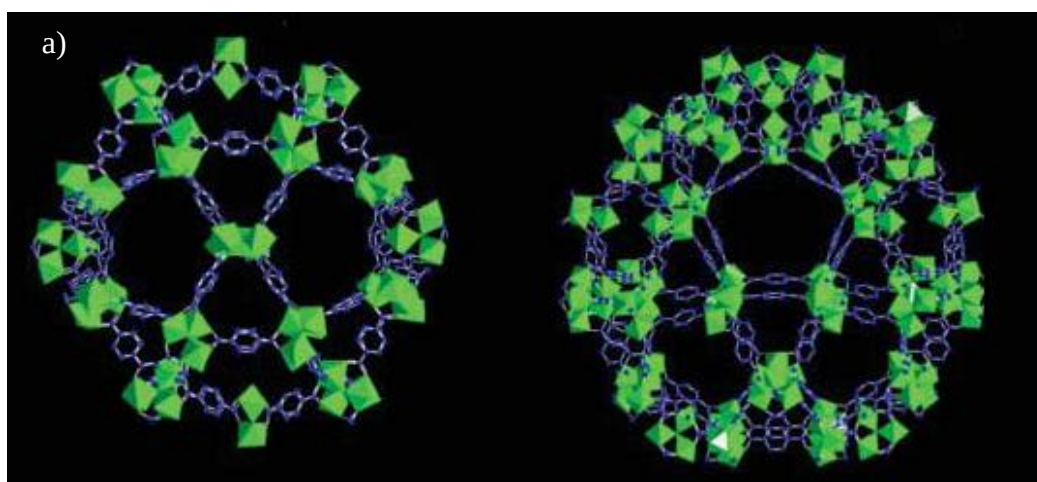


Fig. 2.2 Gas adsorption isotherms for MIL-53(Cr) (open squares – CO₂, filled circles – CH₄). Figure taken from reference 32.

Another example of a stable MOF constructed from M(III) cations is MIL-101 which consists of Cr(III) nodes.³¹ This material was synthesised *via* a hydrothermal reaction between 1,4-benzene dicarboxylic acid and Cr(NO₃)₃ in the presence of HF to give Cr₃F(H₂O)₂O[(O₂C)-C₆H₄-(CO₂)]₃. Each Cr centre is bonded to 4 O atoms from the dicarboxylate ligands, one μ₃-O atom and one H₂O or F from the reaction medium which can be removed after activation leaving an open coordination site. These octahedra are connected through μ₃-O

centres to form trinuclear Cr_3O building units. The trinuclear units are bridged by ligands to form mesoporous cages with large hexagonal (16, 14.7 Å diameter) and pentagonal (12 Å diameter) windows. These large cages lead to a large internal surface area estimated to be $\sim 5900 \text{ m}^2 \text{ g}^{-1}$ (Langmuir S.A), one of the highest surface areas recorded for a MOF. It has a moderate thermal stability, decomposing above 500 K and has been shown to be stable in various organic solvents. MIL-101(Cr) displays high CO_2 adsorption capacity, reaching 8.0 mmol g^{-1} at 283 K and 5 bar.³² It was found that adsorption capacity increases with increased polarizability of the guest molecules due to interactions with the Lewis acidic sites of free Cr(III).



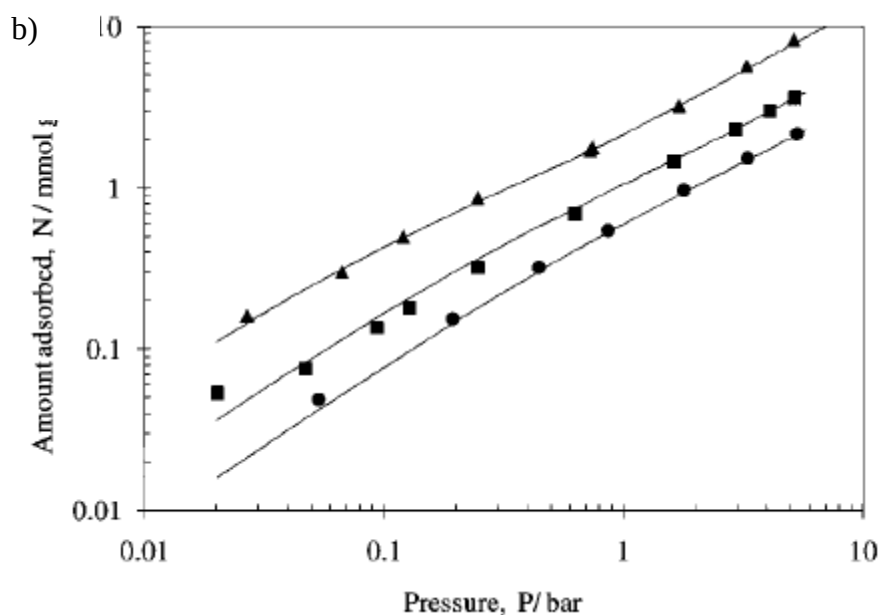


Fig. 2.3 a) Structure of MIL-101 showing the two types of mesoporous cage found within the structure. Figure taken from reference 31. **b)** CO₂ adsorption uptakes for MIL-101 (triangles – 283 K, squares – 319 K, circles – 351 K, line – dual site Langmuir model). Figure taken from reference 32.

2.1.2 NOTT-300(Al)

NOTT-300(Al), [Al₂OH₂(L)] (H₄L = biphenyl-3,3',5,5'-tetracarboxylic acid), was first reported by the Nottingham group in 2012 and was found to possess interesting structural features including helical chains of Al octahedra, high thermal stability and a high CO₂ and SO₂ uptake.³³ NOTT-300(Al) is also stable to water after activation, which is often not the case for many M(II) MOFs. This makes the material suitable for CO₂ separations as H₂O vapour is present in flue gas; water stability is crucial for a material to be considered for this application. The structure of NOTT-300(Al) consists of chains of AlO₆ octahedra linked by the fully deprotonated ligand. Each Al(III) centre is coordinated to six oxygen atoms, four from carboxylates and two from μ_2 -OH groups. Unlike in MIL-53(Al), these bridging –OH groups are in mutually *cis* positions and this

causes the AlO_6 chains to be helical (Fig. 2.4). One thing to be noted about the structure is the protrusion of the $-\text{OH}$ groups into the pores.

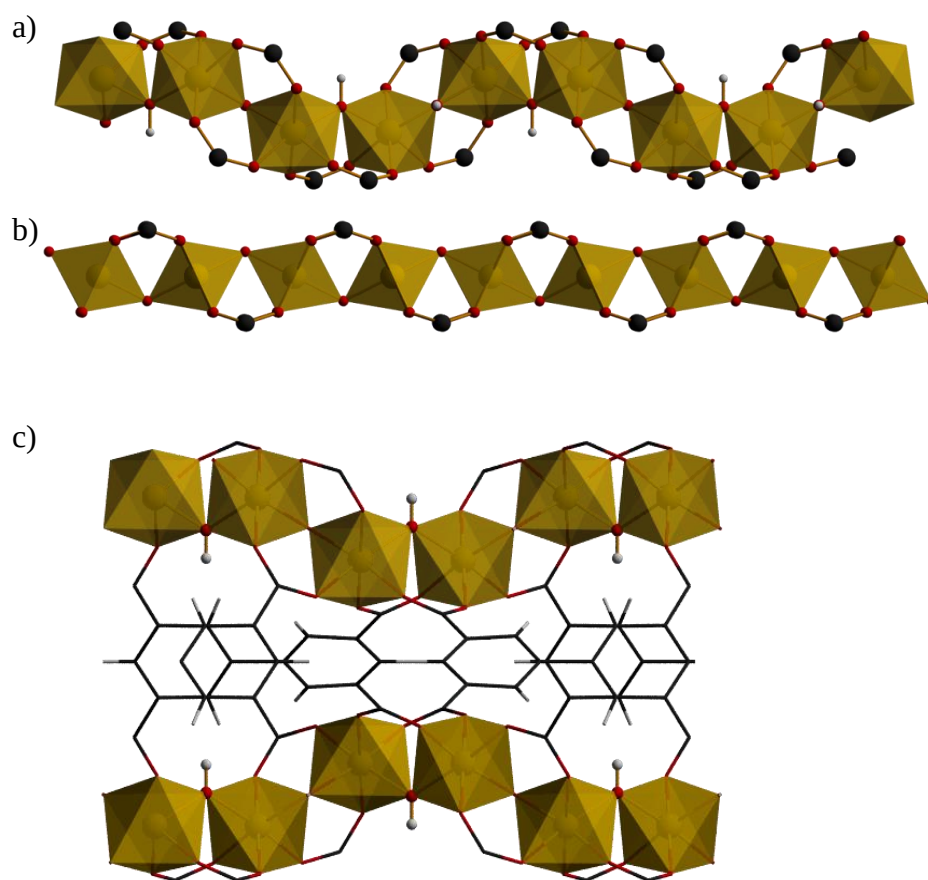


Fig. 2.4 Comparison of the different $[\text{AlO}_4(\text{OH})_2]$ chains caused by μ_2 -OH groups in **a)** NOTT-300(Al) (*cis* μ_2 -OH), **b)** MIL-53(Al) (*trans* μ_2 -OH).²⁰ **c)** Structure of NOTT-300(Al) showing protrusion of OH groups into pores, the $-\text{OH}$ groups are highlighted in ball and stick mode (Al – yellow, oxygen – red, carbon – grey, hydrogen – white, $[\text{AlO}_4(\text{OH})_2]$ – yellow octahedron).

To understand the high affinity this material possesses towards CO_2 , *in situ* PXRD, INS and DFT experiments were combined to visualise the dynamics of the captured gas molecules within the framework.³³ CO_2 is typically difficult to study using neutrons as the cross sections for C and O are too small, 5.551 barns and 4.232 barns, respectively.³⁴ However, the interactions between CO_2 and the

framework can still be investigated using this method by monitoring the dynamics of the H atoms within the framework structure, such as the bridging OH and H in benzene rings, as a function of CO₂ loading. The INS spectra of NOTT-300(Al) and NOTT-300(Al)·1.0CO₂ showed two major increases in peak intensity, indicating clear interactions between CO₂ and the framework hydrogen atoms.

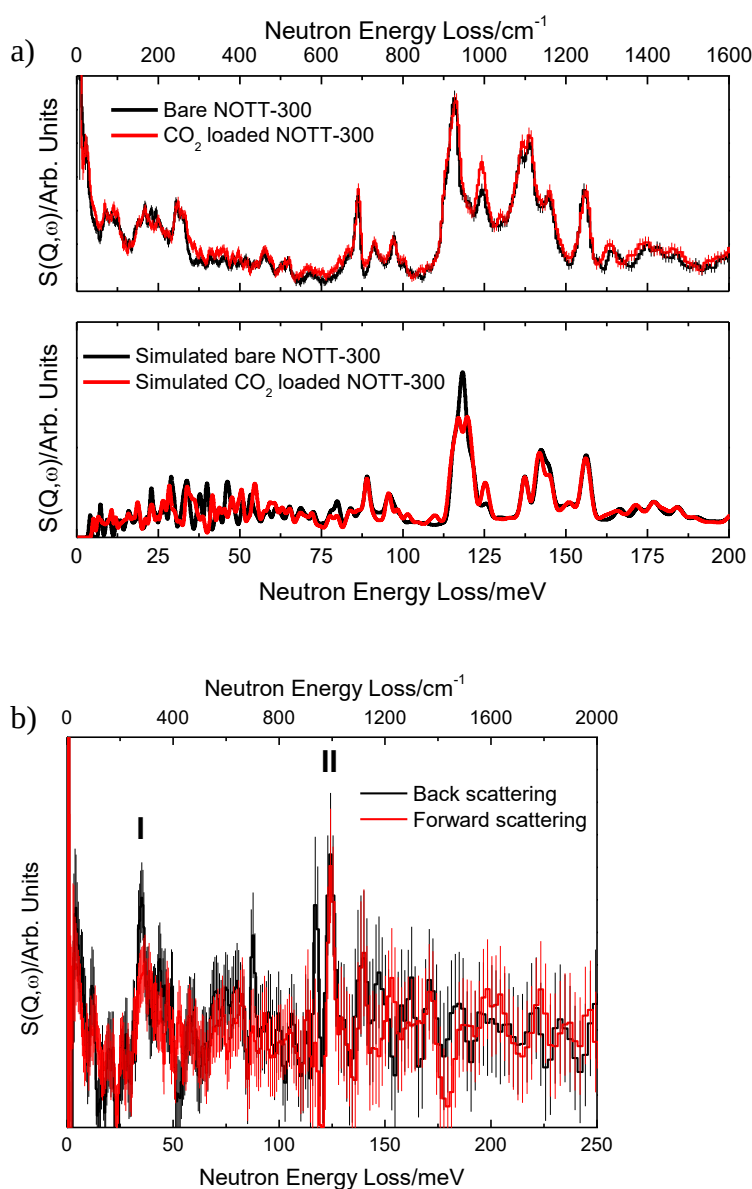


Fig. 2.5 INS spectra recorded for NOTT-300(Al). **a)** Comparison of recorded INS spectra (top) and simulated INS spectra (bottom) for bare and CO₂ loaded NOTT-300(Al). **b)** Difference

spectra for CO₂-loaded NOTT-300(Al) with the two peaks highlighted. The difference spectra were calculated by subtracting the spectrum of bare NOTT-300(Al) from the spectrum of CO₂-loaded NOTT-300(Al). Figures taken from reference 33.

Peak I occurs at low energy transfer (30meV) and peak II occurs at high energy transfer (125meV). To understand these changes in peak intensity DFT calculations were carried out. It was shown that the change in peak I was caused by the O-H groups wagging perpendicularly to Al-O-Al direction in the presence of CO₂. Peak II is attributed to the wagging of the four CH aromatic hydrogens on four benzene rings that are adjacent to each CO₂. These calculations show that there are five hydrogen atoms that interact cooperatively with the O(δ^-) charge centres of CO₂ *via* weak to moderate hydrogen bonds and supramolecular interactions. *In situ* PXRD measurements confirm this interaction between CO₂ and the hydroxyl groups.

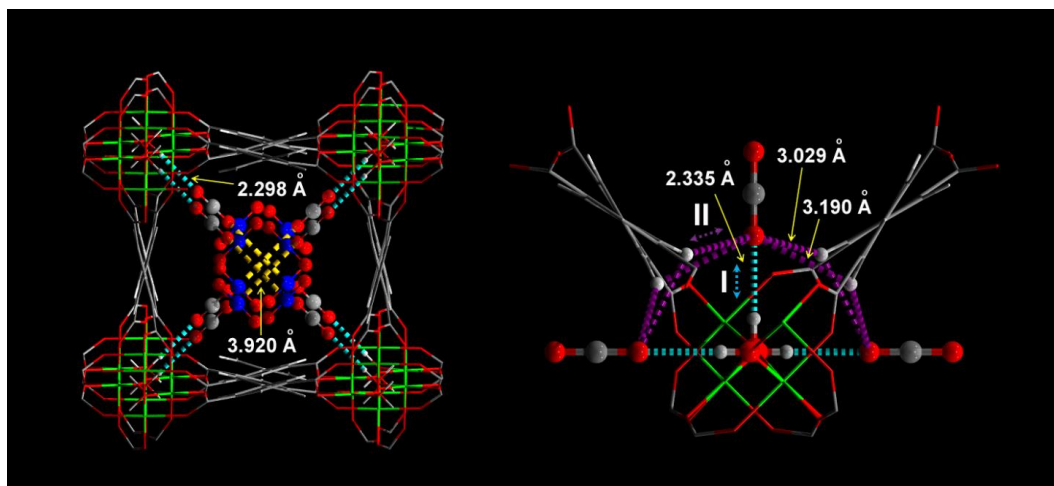


Fig. 2.6 Visualisation of CO₂ in the channels of NOTT-300(Al) showing the H-bonds between CO₂ (I) and the OH group (cyan), CO₂ and aromatic hydrogens (purple) and between the two CO₂ molecules (yellow, the C atom on CO₂(II) highlighted in blue). Figure taken from reference 33.

Owing to the high CO₂ adsorption capacity and selectivity demonstrated by NOTT-300(Al) the aim of this work is to synthesise a Cr(III) containing analogue of NOTT-300 and investigate how the change in metal centre affects the gas adsorption properties.

2.2 Results and Discussion

2.2.1 Synthesis and structure of NOTT-300(Cr)

NOTT-300(Cr) was initially synthesised using the same conditions as NOTT-300(Al); however, the reproducibility of the product was lower than that for the Al(III) material. Cr(III) is more chemically inert than Al(III), and therefore a more acidic reaction medium and longer reaction times were selected to aid the self-assembly process. NOTT-300(Cr) can be successfully prepared under a variety of synthetic conditions shown in Table 2.1. Increasing the quantity of acid was found to lead to a more reproducible synthesis. However, even the best synthetic conditions were not entirely reproducible and could still produce a completely amorphous product.

	Type of Acid	Amount of Acid (ml)	Piperazine (g)	Water (ml)	Reaction time (days)	Product
1	HNO ₃ (2.8 M)	2	0.10	10	3	Yes, low crystallinity
2		3	0.07		4	Yes
3		3	0.07	10	5	Yes, no improvement from 4→5 days
4	HCl (2.6 M)	2	0.10	10	4	Yes
5		2	0.00	10	4	No
6		3	0.07	10	4	Yes

Table 2.1 Details of the different synthetic conditions trialled for the synthesis of NOTT-300(Cr).

As none of these synthetic conditions resulted in the formation of single crystals,

X-ray powder diffraction was used to determine the structure of NOTT-300(Cr) and was also used as a screening process for the crystallinity and purity of the material. High-resolution PXRD was carried out using synchrotron radiation at Beamline I11 at Diamond Light Source. NOTT-300(Cr) crystallises in tetragonal space group $I4_122$ and displays similar PXRD pattern to its Al(III) analogue with a slight cell expansion thus confirming the isostructural nature of these frameworks.

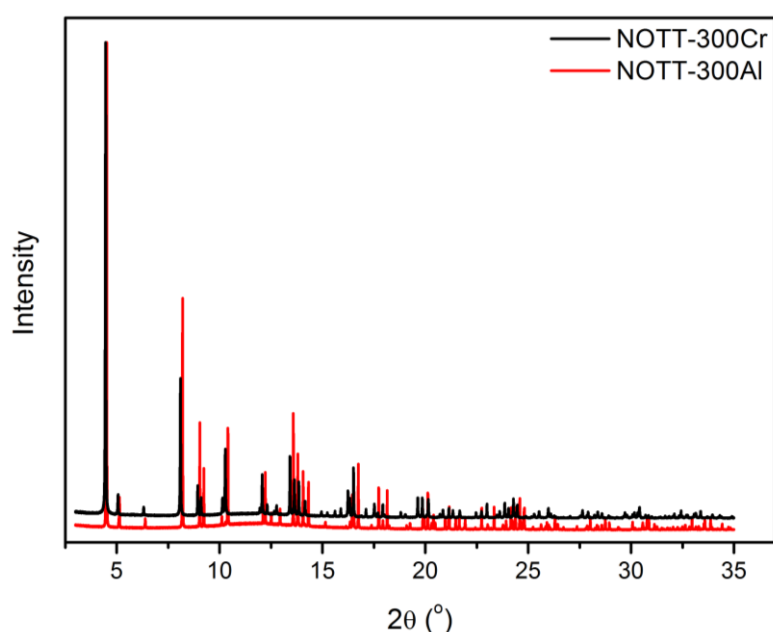


Fig. 2.7 PXRD pattern for NOTT-300(Cr) (λ - 0.825633 Å) and comparison with NOTT-300(Al) (λ -0.826949 Å).

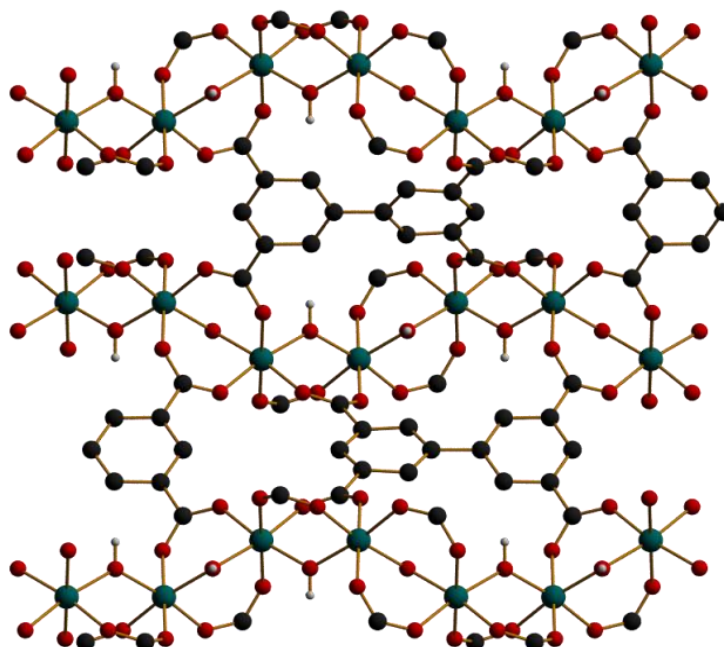
	$a = b$ (Å)	c (Å)	Cell volume (Å ³)
NOTT-300(Cr)	14.99(2)	11.95(1)	2694.44(2)
NOTT-300(Al)	14.82(3)	11.77(3)	2589.50(2)

Table 2.2 The unit cell parameters for NOTT-300(Al) and NOTT-300(Cr).

The structure was refined using Rietveld method which confirmed the presence of chains of CrO₆ octahedra linked through the fully deprotonated L⁴⁻ to form a 3D network, with 1D pores running along the c axis. There is a slight increase in pore diameter when compared to NOTT-300(Al), 6.8 x 6.8 Å vs. 6.5 x 6.5 Å.

Each Cr(III) is coordinated to six oxygen atoms, four from the carboxylate groups on the ligand ($\text{Cr—O(2,3)} = 1.974(1)$ and $1.961(1)$ Å) and two from bridging hydroxyl groups ($\text{Cr—O(1)} = 1.952(1)$ Å). The bridging $\mu_2\text{-OH}$ groups are in *cis* configuration around the Cr(III) ion, leading to a helical chain of $[\text{CrO}_6]$ in the *c* direction, with the -OH groups protruding directly into the pores. It is these protruding OH groups that give a direct site for guest-host interaction through H bonds, which contributes towards the high CO_2 uptake in the NOTT-300(Al) analogue. The differences in size and electronic nature between Al(III) and Cr(III) lead to small changes in the framework structure, specifically the M-OH bond lengths and strength. These differences will affect how the guest molecules interact with the framework, which in turn affects substrate uptake at lower pressures. The different bond lengths for both NOTT-300(Al) and NOTT-300(Cr) are summarised in Table 2.3 below.

a)



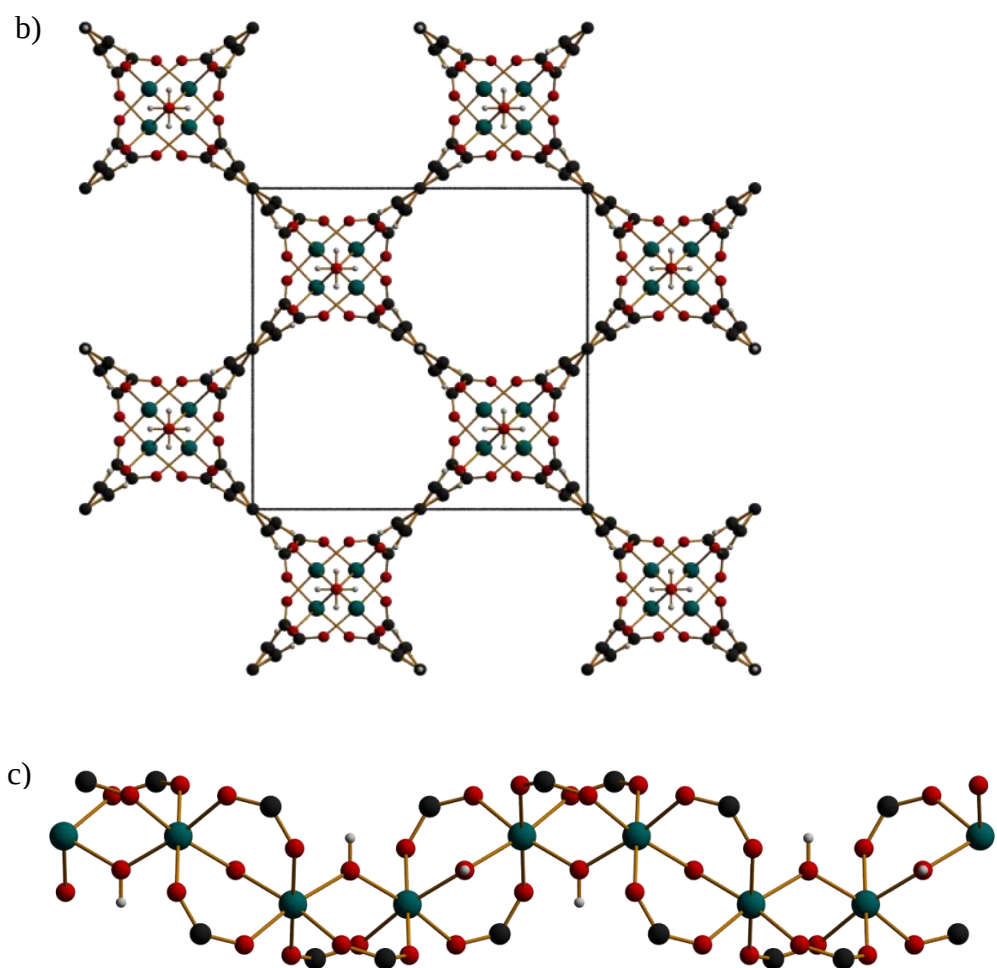


Fig 2.8 View of the crystal structure of NOTT-300(Cr) (Cr – teal, oxygen – red, carbon – grey, hydrogen – white) showing **a)** view along *a* axis showing packing of Cr chains, **b)** view along *c* axis showing porous nature of material, with the unit cell highlighted, and **c)** helical chain of corner sharing CrO₆ octahedra.

	NOTT-300(Cr) (Å)	NOTT-300(Al) (Å)
M—O1 (μ_2 -OH)	1.952(1)	1.930(1)
M—O2	1.974(1)	1.935(1)
M—O3	1.961(1)	1.929(2)

Table 2.3 Comparison of the M—O bond lengths in NOTT-300(Cr) and NOTT-300(Al).

2.2.2 Thermal stability of NOTT-300(Cr)

The uncoordinated water molecules that occupy the pores of the as-synthesised NOTT-300(Cr) can be easily removed by heating at 110 °C under vacuum (10^{-7}

bar) or under flow of N₂ gas confirmed by thermogravimetric analysis (TGA) which shows that the as-synthesised sample loses solvent up to 180 °C. The solvent lost is a mixture of water (residual from synthesis) and acetone (used to wash and store the sample). The loss of solvent corresponds to ~22 % mass, which is similar to that for NOTT-300(Al) (~20 %). After the initial solvent loss, the framework remains stable up to ~ 450 °C. This is a higher decomposition temperature than that for NOTT-300(Al) by approximately 50 degrees.

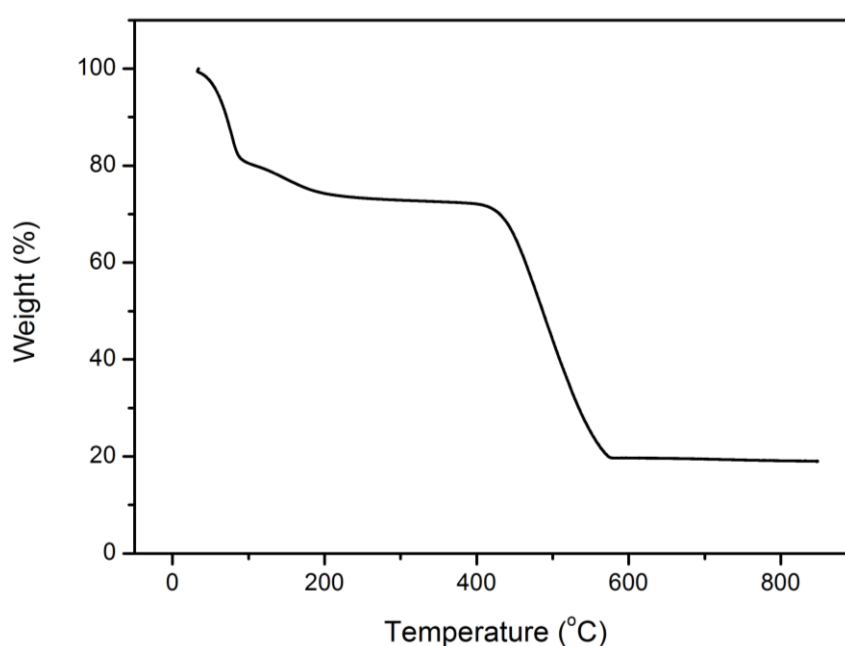
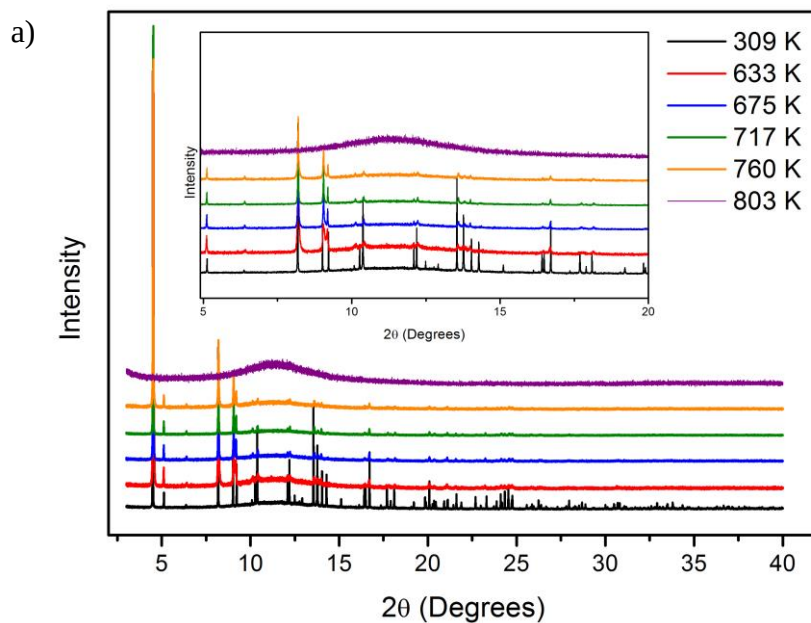


Fig. 2.9 TGA trace for NOTT-300(Cr) after acetone wash under N₂ atmosphere with 5 °C a minute temperature ramp.

The thermal stability of both NOTT-300(Al) and NOTT-300(Cr) were further studied using variable temperature PXRD to monitor the changes of the framework structure with increasing temperature. There is a clear difference in the behaviour of the two MOFs on increasing temperature. NOTT-300(Al) displays clear sharp peaks at room temperature, with distinguishable peaks up to 35/37 °. These high angle peaks are lost on going to 633 K; however, there are discernible peaks observed to ~ 25 ° at all temperatures recorded, indicating the

majority of the framework is still intact. Full decomposition of the product occurs between 760 K and 803 K. NOTT-300(Cr) also decomposes in that temperature window but it can be seen that NOTT-300(Cr) displays a more resolved pattern at higher temperatures. There are observable peaks above 30° even at 717 K. Although both materials decompose in the same temperature window (760 – 803 K) NOTT-300(Cr) appears to have the higher thermal stability, as supported by TGA, and retains its crystallinity at high temperature, as measured by PXRD.



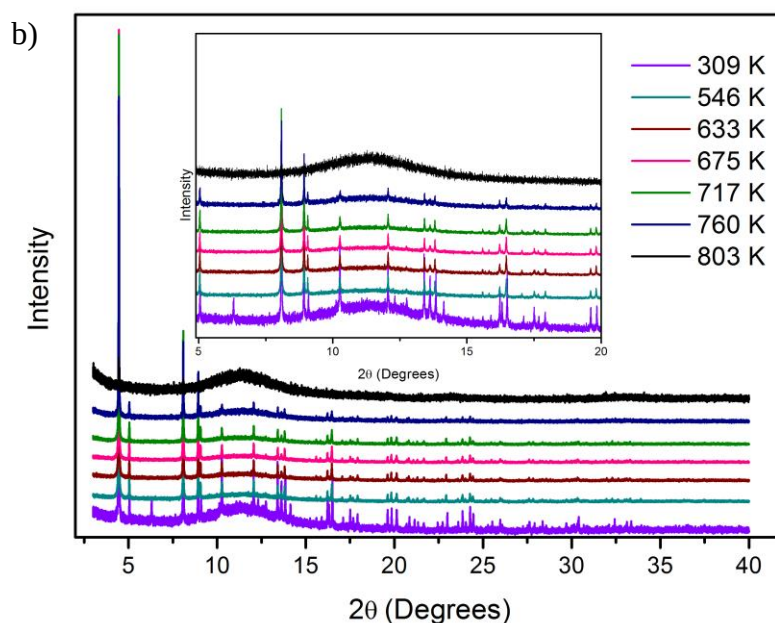


Fig. 2.10 High temperature PXRD patterns for **a)** NOTT-300(Al) and **b)** NOTT-300(Cr) $\lambda=0.825690$.

Indexing of these patterns allows us to see how the unit cells of these frameworks behave with increasing temperature. Both frameworks exhibit similar behaviours with an initial contraction of the unit cell along the a and b axes, which is accompanied by an expansion of the unit cell along the c axis. This initial contraction is only small and is due to solvent loss from the pores. NOTT-300(Al) exhibits a larger contraction (0.3%) compared to that of NOTT-300(Cr) (0.04%) indicating the NOTT-300(Al) sample contained more solvent and is more flexible. Upon further heating the Al(III) framework expands slightly along the a axis, with NOTT-300(Cr) not appearing to change significantly. The overall behaviour of the two MOFs is similar; however, there are some important differences. The differences in unit cell dimensions/amount of contraction/expansion are much larger for the NOTT-300(Al) material than

for NOTT-300(Cr). This could account for the loss of the higher angle peaks for NOTT-300(Al) at high temperature.

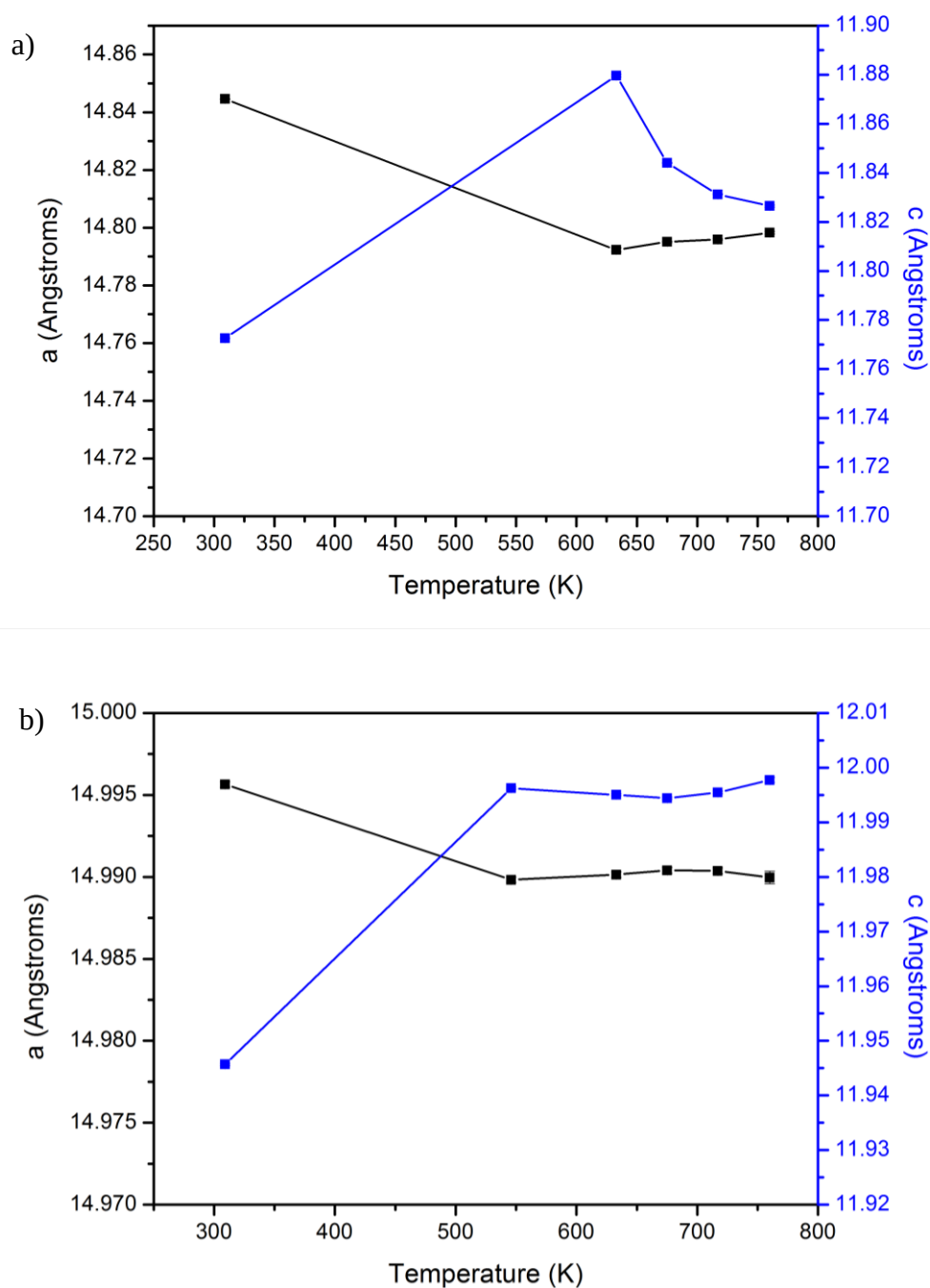


Fig. 2.11 Changes in unit cell parameters as a function of temperature for **a)** NOTT-300(Al) and **b)** NOTT-300(Cr).

2.2.3 H₂ and N₂ Adsorption

H₂ and N₂ adsorption isotherms were carried out at 77 K between 0-1 bar (N₂) and 0-20 bar (H₂) for desolvated NOTT-300(Cr) (Fig. 2.12). The N₂ isotherm displays a rapid uptake up to 3.18 mmol g⁻¹ (71.2 cc g⁻¹) at 0.1 bar. As the pressure increases further the uptake increases more gradually to a maximum adsorption of 4.37 mmol g⁻¹ (97.9 cc g⁻¹) at 1 bar. The H₂ isotherm shows a moderate uptake at 77 K reaching 14.1 mmol g⁻¹ at 20 bar. There are many MOFs reported in the literature with higher H₂ uptakes, such as NOTT-103 a Cu(II) framework (32.55 mmol g⁻¹).³⁵ There is also a large hysteresis upon desorption, which may be a result of the slow diffusion of the gas at this temperature as all gas is removed upon heating to room temperature. Both H₂ and N₂ uptakes are higher than those for NOTT-300(Al), 0.3 mmol g⁻¹ and 0.7 mmol g⁻¹ (16 cc g⁻¹) respectively, which corresponds to only surface adsorption. It is thought the low N₂ and H₂ adsorption observed in NOTT-300(Al) at these temperatures is due to limited diffusion along the narrow pores. Therefore, it can be seen that the change in metal centre to Cr(III) and its resulting effects on structure, such as increased pore size, can have a large affect on the gas adsorption properties of the framework.

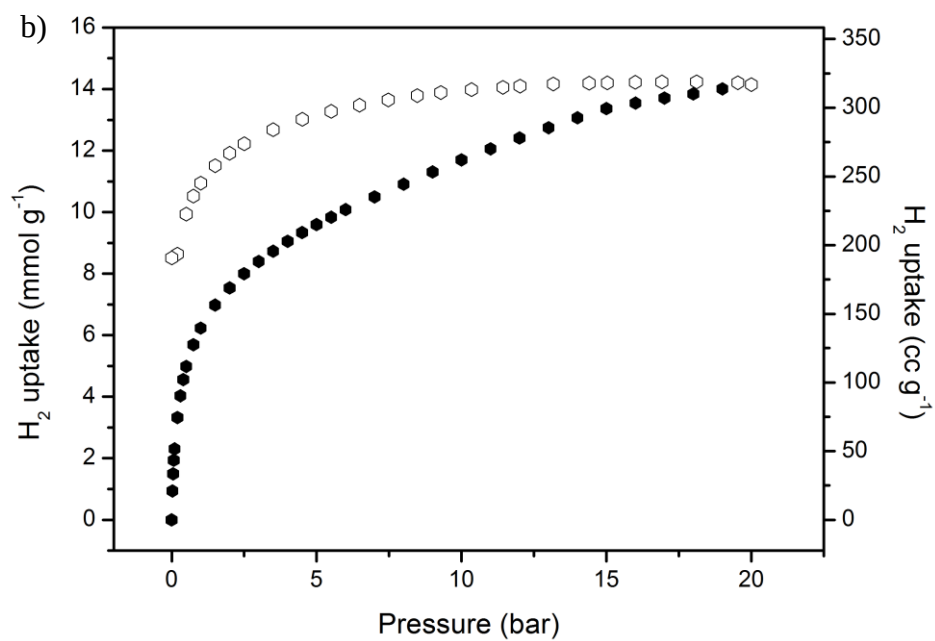
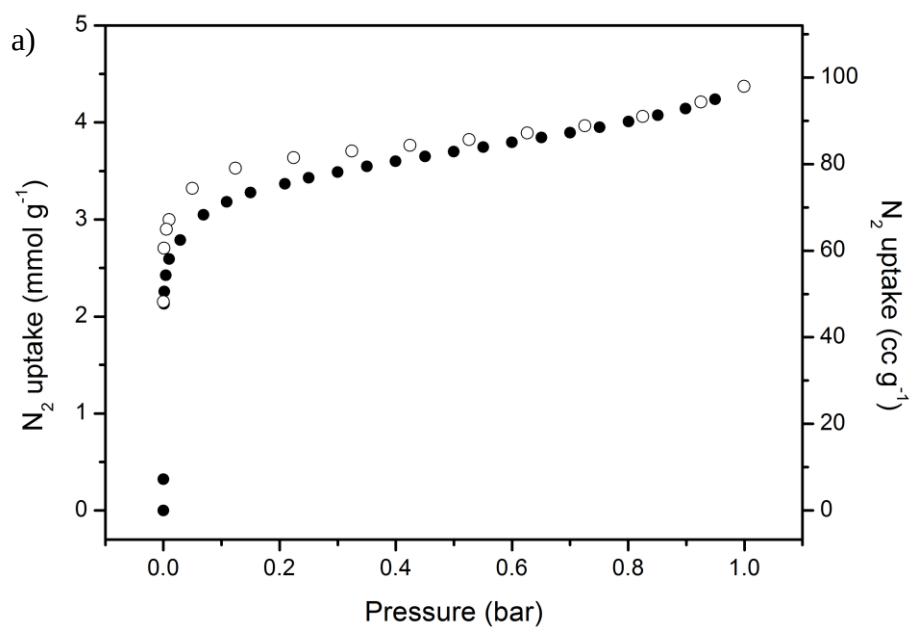


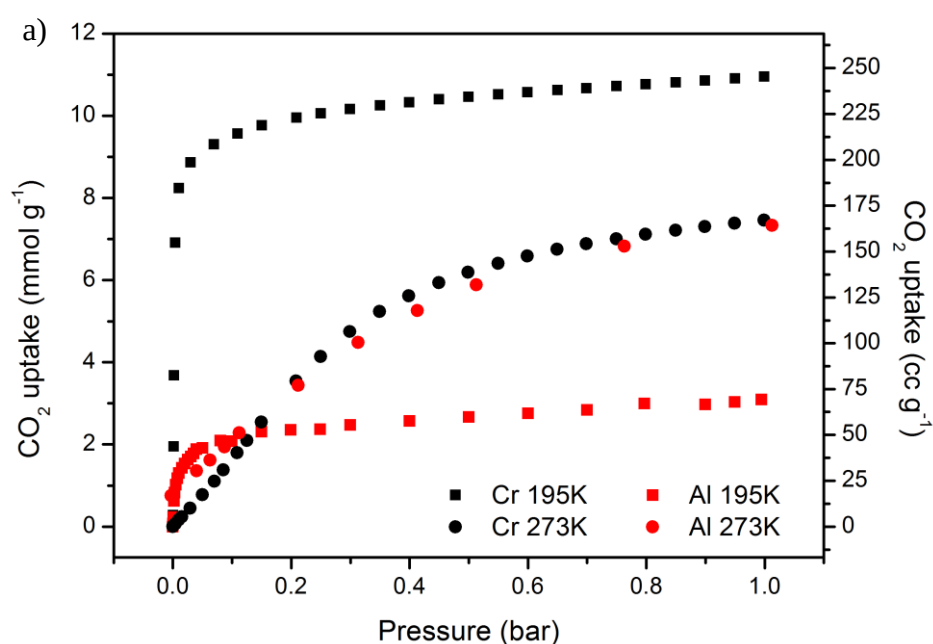
Fig. 2.12 Gas adsorption isotherms for NOTT-300(Cr) **a)** N_2 at 77 K and **b)** H_2 at 77 K (filled shapes – adsorption, open shapes – desorption).

2.2.4 CO₂ Adsorption

The potential of NOTT-300(Cr) for CO₂ storage/separation was assessed by carrying out CO₂ adsorption isotherms at several temperatures, 195 K (0 - 1 bar) and 273-333 K (0 - 20 bar) (Fig. 2.13). The material displays a high affinity for CO₂ adsorbing 10.95 mmol g⁻¹ at 195 K and 1 bar. The isotherm shows a rapid uptake at low pressures, reaching 9.57 mmol g⁻¹ at 0.1 bar. Above 0.1 bar NOTT-300(Cr) adsorbs CO₂ less rapidly, reaching a plateau at 10.95 mmol g⁻¹. The isotherms recorded at higher temperatures (273 - 333 K) display the same type-I shape, with the majority of the uptake taking place at lower pressures. Upon increase in temperature (195 to 273 K) the total uptake is reduced, as expected. However, the total uptake still remains high reaching 10.08 mmol g⁻¹ at 273 K and 20 bar. Even at 1 bar the high uptake capacity is maintained, at 7.46 mmol g⁻¹, and is comparable to some of the leading literature MOFs such as MgMOF-74 (~9 mmol g⁻¹),³⁶ NOTT-300(Al) (7 mmol g⁻¹) and HKUST-1 (~8 mmol g⁻¹).³⁷ As expected, the CO₂ uptake decreases with increasing temperature from 273 – 333 K (10.08 – 7.98 mmol g⁻¹ at 20 bar), but there is no significant drop in uptake even at 333 K which indicates a high affinity for CO₂.

NOTT-300(Cr) has a higher CO₂ adsorption capacity than NOTT-300(Al) at all temperatures at 20 bar. This could be due to the larger size of NOTT-300(Cr) allowing more space for more CO₂ uptake. At lower pressures (1 bar), where the interaction between adsorbent/adsorbate plays a more important role in uptake than available space, NOTT-300(Cr) still exhibits a higher uptake of CO₂ than NOTT-300(Al). This indicates that both strong adsorbent/adsorbate interactions and increased available space contribute to the higher CO₂ uptake capacity for the Cr(III) material. However, it can be seen in the isotherm at pressures below

0.15 bar that NOTT-300(Al) has a higher CO₂ adsorption than NOTT-300(Cr), 2.64 mmol g⁻¹ and 2.54 mmol g⁻¹ respectively, possibly indicating at very low pressures the interaction between the framework and the CO₂ molecules is stronger for Al(III) or that NOTT-300(Al) has slightly narrower pores than NOTT-300(Cr). The adsorption behaviour of these two materials at ambient temperatures are similar; however, the CO₂ isotherms measured at 195 K display significant differences with NOTT-300(Al) adsorbing very little, 2.95 mmol g⁻¹, compared to the increased adsorption for NOTT-300(Cr) reaching 10.95 mmol g⁻¹. The higher CO₂ adsorption capacity in NOTT-300(Cr) at 195 K can be partially explained by the increase in pore diameter, making the energy barrier for diffusion lower.



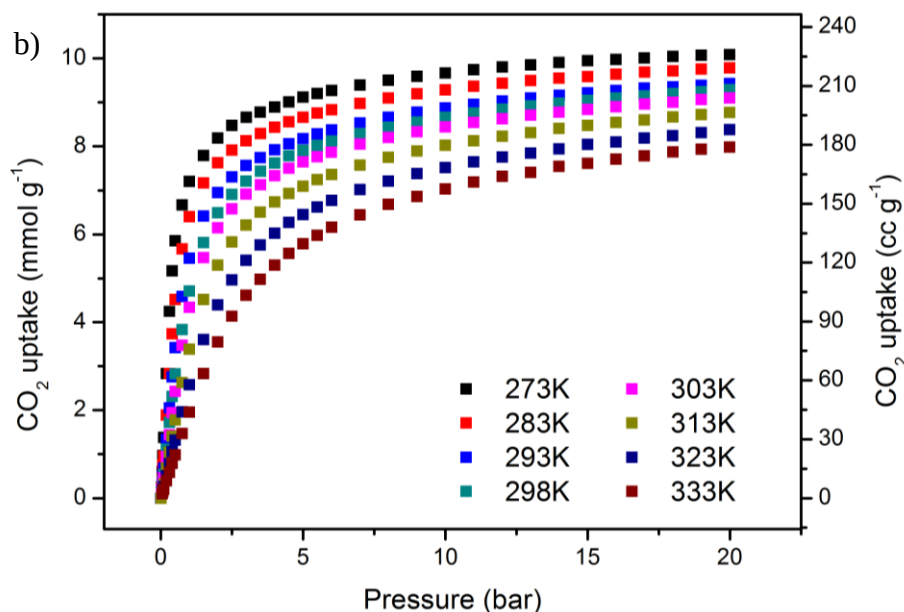


Fig. 2.13 Gas adsorption isotherms recorded for NOTT-300(Cr) **a)** CO₂ adsorption isotherms at 195 K (squares) and 273 K (circles) to show difference in adsorption behaviour between NOTT-300(Cr) (black) and Al (red), **b)** All recorded CO₂ adsorption isotherms from 0 – 20 bar for NOTT-300(Cr).

	195 K	273 K	283 K	293 K	298 K	303 K	313 K	323 K	333 K
Cr	10.95	10.08 (7.46*)	9.78	9.42	9.23	9.09	8.77	8.38	7.98
Al	2.95	9.49 (7.00*)	7.33	7.29		7.13			

Table 2.4 CO₂ uptakes for NOTT-300(Cr) and NOTT-300(Al) (195 K – 1bar, 273–333 K – 20 bar). *1 bar uptakes.

The isosteric heat of adsorption was calculated using the van't Hoff isochore on the data from the CO₂ adsorption isotherms measured at 273–333 K.

$$\ln P = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (2.1)$$

Where P is the pressure in Pa, T is the temperature in K and R is the ideal gas constant. The heat of adsorption for this material is moderate; ~24 kJ mol⁻¹ at initial loading and then steadily increases with increased loading to a maximum heat of adsorption of ~32 kJ mol⁻¹ at an uptake of 9.5 mmol of CO₂ per gram of

material. This moderate heat of adsorption is expected as the interactions between the framework and the CO₂ molecules are likely to be based upon relatively weak H-bonds and van der Waals interactions. Compared to the heat of adsorption for amine absorbents which is much higher (MEA – 80-100 kJ mol⁻¹)³⁸ as carbamate bonds are formed. A lower heat of adsorption is crucial for low energy regeneration of the adsorbate material and thus provides an “easy on/easy off” mechanism in which complete regeneration of the MOF material is achieved. The entropy steadily decreases with increased loading of CO₂ in NOTT-300(Cr) as expected reflecting the CO₂ molecules filling the “binding” sites and forming inter-molecular interactions, and thus becoming more ordered. The isosteric heat of adsorption is comparable to MOFs in the literature with similar uptakes.³⁹ An increased heat of adsorption at low loadings indicates strong interactions between the guest molecules and the framework. Further increase in heat of adsorption with increased loadings indicates strong inter-molecular interactions between the CO₂ molecules. High heat of adsorption is not always a beneficial property as the material will not be economically viable if regeneration costs are similar to those for the separation methods in place already.

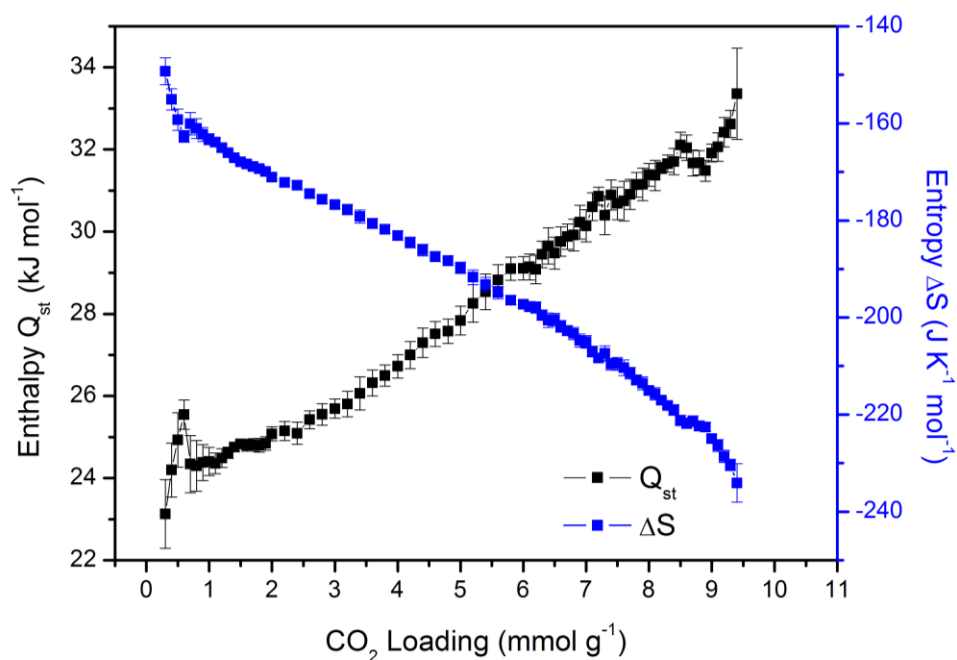


Fig. 2.14 Variation in heat of adsorption (Q_{st}) and entropy (ΔS) for CO₂ adsorption in NOTT-300(Cr).

Another indication that the initial interactions between the framework and the CO₂ molecules are stronger in NOTT-300(Al) than NOTT-300(Cr) is the heat of adsorption at low loadings. NOTT-300(Al) has a higher heat of adsorption at initial loadings than NOTT-300(Cr) with values of 27.5 kJ mol⁻¹ and 24 kJ mol⁻¹, respectively. Both MOFs display the same trend, with the heat of adsorption increasing with increasing CO₂ loadings but with NOTT-300(Al) consistently remaining higher than NOTT-300(Cr). This indicates the interactions between CO₂/framework and CO₂/CO₂ (at higher loadings) are stronger in NOTT-300(Al) than in NOTT-300(Cr). However, they are still sufficiently strong in NOTT-300(Cr) to facilitate high CO₂ adsorption.

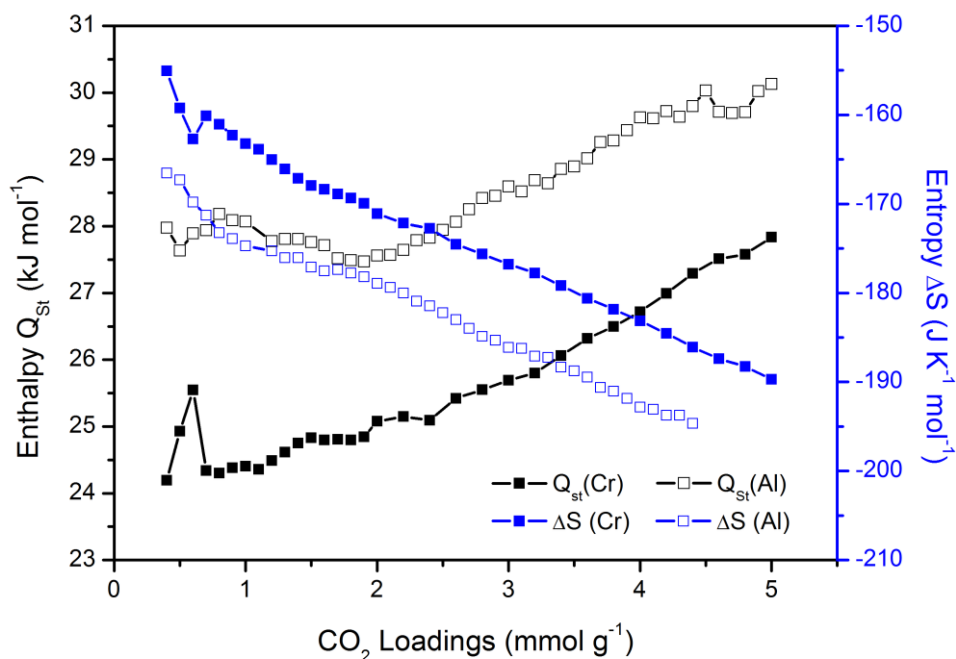


Fig. 2.15 Comparison of the heat of adsorption (Q_{st}) and entropy (ΔS) for CO_2 adsorption in NOTT-300(Cr) and NOTT-300(Al).

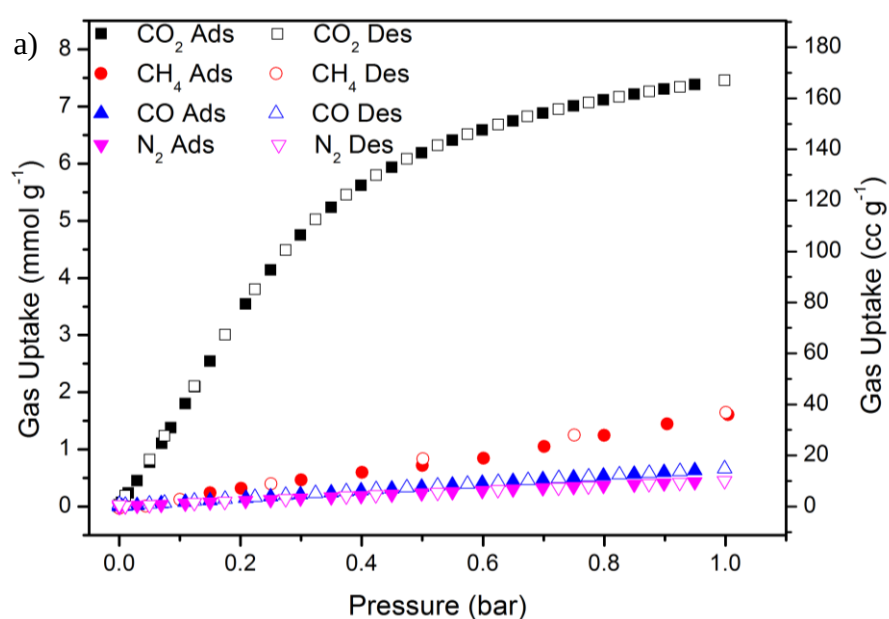
2.2.5 Adsorption of CH_4 , CO and N_2

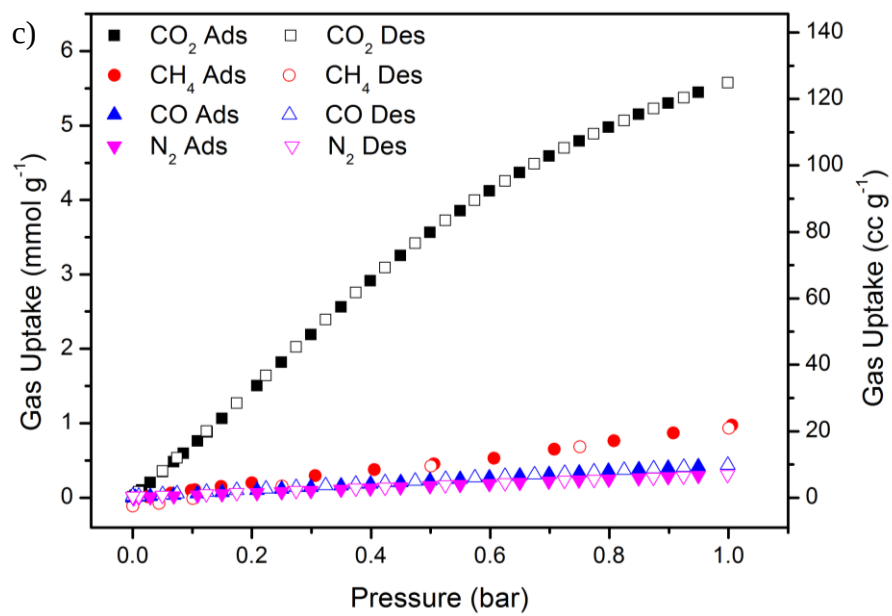
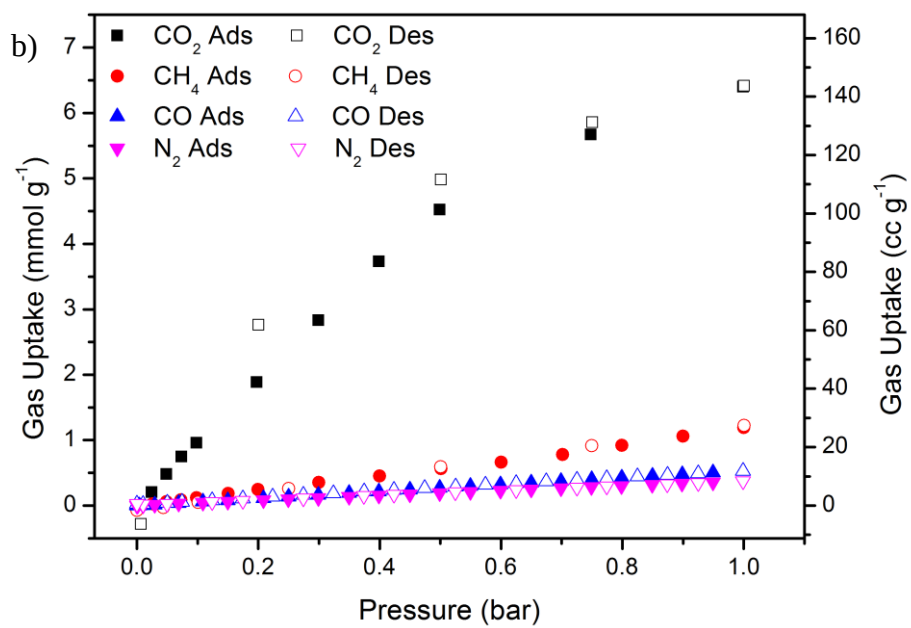
Adsorption isotherms were also measured for CH_4 , CO and N_2 under similar conditions (273 – 303 K) in order to fully assess the gas adsorption properties of the material. CH_4 shows the highest adsorption at all temperatures, with an uptake of 7.18 mmol g^{-1} at 273 K and 20 bar. Although the CH_4 uptake is reasonably high, there are examples in the literature of much higher uptakes, *e.g.* HKUST-1 ($10.04 \text{ mmol g}^{-1}$ at 303 K and 35 bar)⁴⁰ and MgMOF-74 (8.21 mmol g^{-1} at 298 K and 35 bar).⁴¹ A further isotherm was conducted at 195 K between 0 - 20 bar to determine the CH_4 uptake at saturation. The total amount adsorbed under these conditions was 7.04 mmol g^{-1} , which is unexpected as a decrease in temperature usually leads to an increase in adsorption. The isosteric heat of adsorption was calculated to be $15.65 \text{ kJ mol}^{-1}$ at initial loading, increasing

steadily to $19.75 \text{ kJ mol}^{-1}$ with increased loading. This is well within the literature values for other MOFs ($13 - 18.5 \text{ kJ mol}^{-1}$).⁴²

In contrast, each of the room temperature (273 – 303 K) CO and N₂ isotherms show very low uptake, only reaching a maximum of 0.66 mmol g^{-1} and 0.45 mmol g^{-1} respectively at 273 K and 1 bar. CH₄ shows an uptake of 1.6 mmol g^{-1} under these same conditions. All gas uptakes are summarised in Table 2.5.

As with CO₂, NOTT-300(Cr) shows an increased uptake for CH₄ and N₂ compared with NOTT-300(Al). However, the low uptakes of CH₄ and N₂ contribute significantly to the high CO₂ selectivity for NOTT-300(Al). This is potentially an issue as an increase in adsorption of all gases may lead to a decrease in overall selectivity. The combination of small structural changes and difference in electronics at the bridging -OH group leads to large differences in adsorption of CO₂ and other gases found in flue gas (CO, N₂ etc.). The overall increase in space (pore diameter and volume) in NOTT-300(Cr) leads to an increased adsorption capacity for all gases measured thus far.





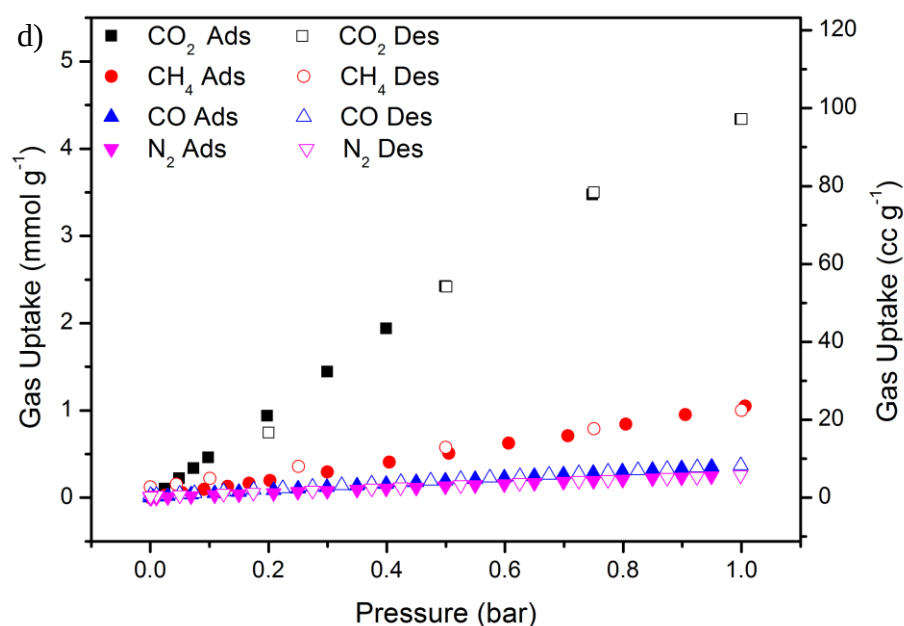


Fig. 2.16 Gas adsorption isotherms for NOTT-300(Cr) measured up to 1 bar at **a)** 273 K, **b)** 283 K, **c)** 293 K and **d)** 303 K.

	195 K (mmol g ⁻¹)	273 K (mmol g ⁻¹)	283 K (mmol g ⁻¹)	293 K (mmol g ⁻¹)	303 K (mmol g ⁻¹)
CO ₂	10.95	7.46 (10.08)	6.40 (9.78)	5.57 (9.42)	4.34 (8.86)
CH ₄	5.64 (7.04)	1.60 (7.18)	1.22 (6.95)	0.93 (6.52)	1.00 (6.28)
CO	5.11	0.66	0.53	0.44	0.37
N ₂	3.15	0.45	0.37	0.31	0.26

Table 2.5 Gas uptakes recorded at 1 bar, values in () denote 20 bar uptake at the same temperature.

2.2.6 CO₂ selectivity

For a material to be considered for potential use in CO₂ separation applications it needs to possess not only a high CO₂ uptake, but also a high CO₂ selectivity. The selectivity of a material can be calculated, estimated and measured in several ways.^{43,44} The most basic of these is to calculate the ratio of the slope of the pure-component isotherms at low pressures. Although crude, this method does estimate the selectivity of a material reasonably well, as the initial slope of the

isotherms is related to the strength of the interaction between gas and framework and it is differences in these interactions that lead to a selectivity for one particular gas. A better way to do this is to use the Ideal Adsorbed Solution Theory (IAST)⁴⁵ which gives a more accurate estimation of the selectivity based on the single-component isotherms. Table 2.6 compares the values obtained from both selectivity calculations for gas uptake in NOTT-300(Cr). These were calculated directly from the isotherm data for each single gas.

Cr	CO ₂ /N ₂		CO ₂ /CH ₄		CO ₂ /CO	
	Ratio of isotherm slope	IAST	Ratio of isotherm slope	IAST	Ratio of isotherm slope	IAST
273 K	18	84	9	15	24	48
283 K	12	40	6	9	18	26
293 K	11	32	6	8	16	22
303 K	9	29	5	8	12	21

Table 2.6 Calculated CO₂ selectivities for NOTT-300(Cr).

All the selectivities calculated for NOTT-300(Cr) are lower than those reported for NOTT-300(Al). However, the selectivities are still high and indicate the material will be capable of separating CO₂ from a number of gas mixtures.

IAST becomes a difficult analysis to use when the differences between the uptakes are very large, eg the difference between CO₂ and N₂ uptakes since the amount adsorbed of the lower adsorbing gas is often too low to fit the Langmuir adsorption model.

2.2.7 Dual Component Gas Adsorption Isotherms

Another way for selectivity to be measured rather than calculated is to carry out dual-component adsorption isotherms. A series of dual-component adsorption isotherms were measured; CO₂/N₂ (1:1 and 15:85) and CO₂/CH₄ (1:1 and 1:9) under flow mode. In contrast to a typically static adsorption isotherm, the flow

mode enables the gas in the sample station to be constantly refreshed by a flow of the desired mix of gases which ensures the composition of the gases in the chamber remain constant throughout the experiment. IAST was used to predict the uptakes of the dual component isotherm based on the selectivity calculations for the single component isotherm. This method was not used for CO₂/N₂ as the CO₂ adsorption is so much higher and dominates the calculation, so much so that the 1:1 selectivity prediction followed the pure CO₂ isotherm within 5%.

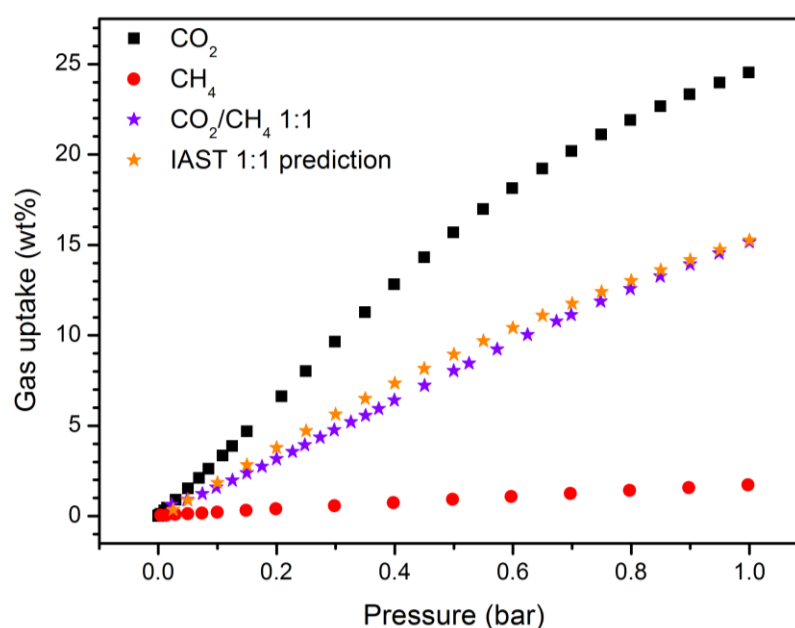


Fig. 2.17 Experimental dual component adsorption isotherm for CO₂/CH₄ 1:1 mixture at 293 K.

The CO₂/CH₄ separation is of importance for the process of natural gas sweetening.³⁶ The CO₂/CH₄ (1:1) flow isotherm reaches a total uptake of 15.16 wt% at 1 bar (Fig. 2.17). When compared to the uptakes of the pure gas isotherm at relevant pressures (0.5 bar), the dual-component uptake is closer to the pure CO₂ isotherm than that for CH₄. CO₂ reaches an uptake of 15.69 wt% at 0.5 bar, whereas CH₄ reaches 0.92 wt% under the same conditions. The IAST prediction closely follows that of the dual component adsorption, which demonstrates the

reliability of the IAST selectivity model. The lower number for the overall uptake indicates that both gases are adsorbed into the framework, as CH₄ is lighter than CO₂. However, there is only a small difference between the dual component isotherm and the pure CO₂ isotherm, leading to speculation that the majority adsorbed gas is CO₂.

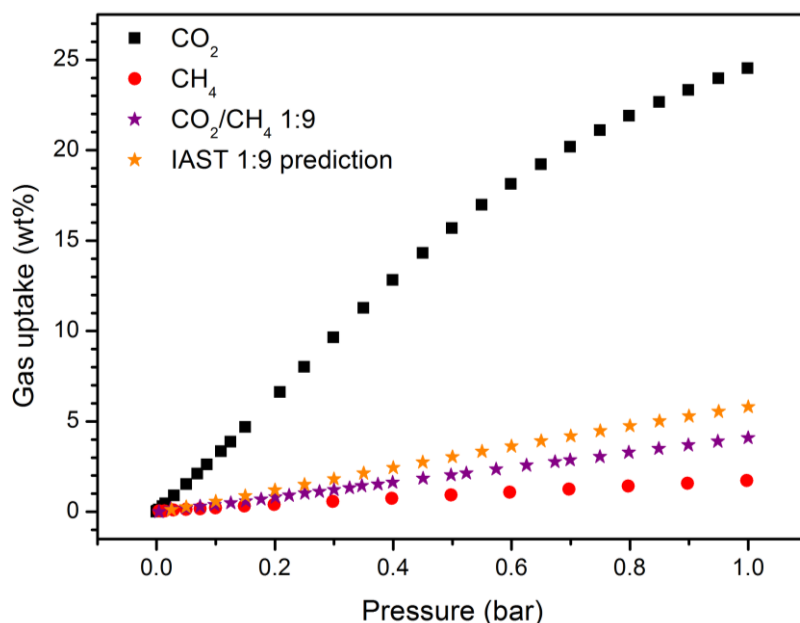


Fig. 2.18 Dual component adsorption isotherm for CO₂/CH₄ 1:9 mixture at 293 K.

At lower CO₂ concentration separation is inevitably more challenging in a 1:9 CO₂:CH₄ mixture compared to CO₂:N₂ as CH₄ can interact with the framework more strongly, albeit weakly, than N₂. With a mix of 9:1 CH₄:CO₂ the total uptake reaches 4.09 wt% at 1 bar (Fig. 2.18). Under these conditions the IAST prediction follows the adsorption closely. However, it does seem to predict a higher CO₂ uptake than is observed based on the higher wt% predicted. At relevant pressures the CO₂ uptake is 3.35 wt% (at 0.1 bar) and CH₄ reaches 1.58 wt% (at 0.9 bar). The higher concentration of CH₄ leads to increased adsorption

of CH₄ and a lower overall selectivity for CO₂. The similar values predicted by IAST clearly shows the material has high selectivity for CO₂ over CH₄ even at low concentrations of CO₂.

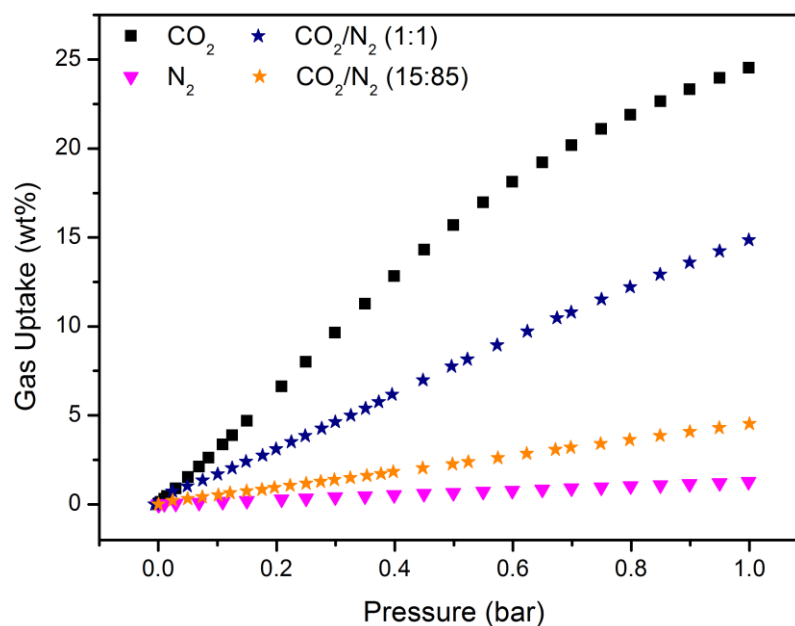


Fig. 2.19 Dual component adsorption isotherms for CO₂/N₂ mixtures.

CO₂/N₂ mixtures were also investigated because of the interest of separating CO₂ from post combustion waste gas streams often comprising of mostly N₂ with CO₂, water vapour and trace amounts of other gases, such as CO. The dual component adsorption isotherm using the equimolar mixture of N₂/CO₂ reaches a total uptake of 14.86 wt% at 1 bar (Fig. 2.19). This is a decrease in uptake from that observed in the pure CO₂ isotherm; at 0.5 bar CO₂ uptake reaches 15.69 wt% and N₂ has an uptake of 0.65 wt% under the same conditions. The reduction in wt% adsorbed indicates that a mix of both gases is adsorbed; however, the high wt% adsorbed clearly indicates it is predominantly CO₂ which is adsorbed. N₂

does not interact with the framework whereas CO₂ forms H-bonds and therefore it is not unreasonable to assume majority gas adsorbed is CO₂.

A mixture of CO₂ and N₂ with concentrations of 15% and 85%, respectively, was chosen because it closely mimics the conditions found in flue gas and is a good “real” test for a low pressure of CO₂ and high pressure N₂ mixture. A total uptake of 4.52 wt% was achieved at 1 bar; this closely resembles the uptake of the pure CO₂ isotherm (4.68 wt%) at relevant CO₂ pressures (0.15 bar) (Fig. 2.19). At the corresponding N₂ pressure (0.85 bar) the uptake reaches 1.09 wt%. Owing to the increased concentration and uptake of N₂, it becomes difficult to estimate how much of the amount adsorbed is CO₂ vs. N₂. It is not expected that full uptake of N₂ is occurring, with the difference in wt% being made up by CO₂ adsorption because of the differences in interaction between the two gases and the frameworks. A good way to look at this is to convert the pressure in the dual component isotherm to the partial pressures of the pure component gas (Fig. 2.20), 0.15 bar for CO₂ and 0.85 bar for N₂, and compare with the pure component adsorption isotherms. When comparing these isotherms, a clear correlation can be seen between the dual component isotherm and the pure CO₂ isotherm. The adsorption behaviour for N₂ is significantly different and so it can be assumed that the majority adsorbed gas is CO₂. Considering the errors in adsorption measurements the uptake is consistent with the pure CO₂ data, suggesting very high selectivity. This clearly displays the high affinity of CO₂ NOTT-300(Cr) under these conditions and the potential for use in CO₂ separation from CO₂/N₂ gas streams.

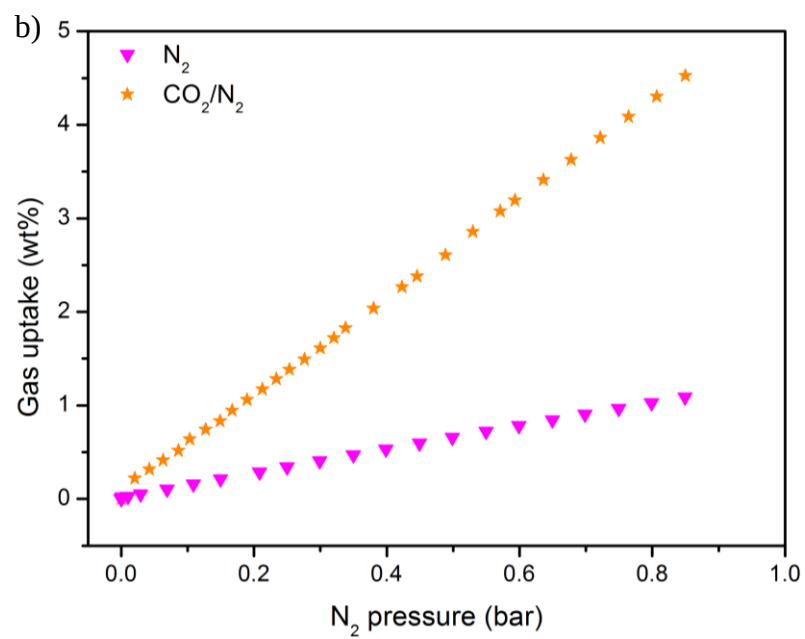
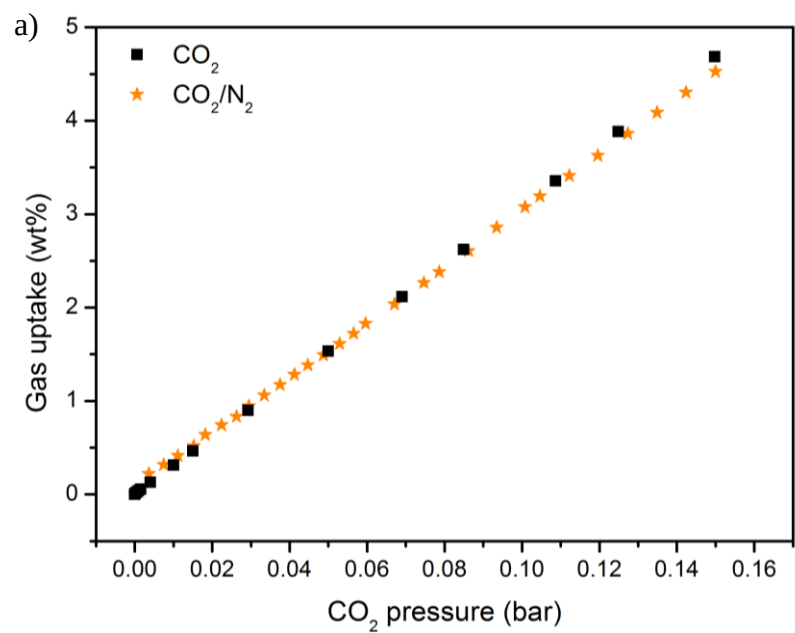


Fig. 2.20 Dual component uptake for CO_2/N_2 (15:85) and single component adsorption at **a)** partial CO_2 pressure, and **b)** partial N_2 pressure.

2.2.8 *In Situ* PXRD analysis of CO₂-loaded NOTT-300(Cr)

The high adsorption of CO₂ within NOTT-300(Cr) indicates the possibility of favourable interactions between CO₂ and the framework. To visualise these interactions and refine the positions of adsorbed CO₂ within the pores, high resolution *in situ* synchrotron PXRD (powder X-ray diffraction) was used. This technique, combined with further probes such as INS (inelastic neutron scattering), has been used previously for NOTT-300(Al).³³ It was discovered that adsorbed CO₂ formed H-bonds with the bridging –OH group which are further reinforced by four C-H...O=C=O van der Waals interactions from the adjacent phenyl rings of the ligand. Similar interactions are expected for CO₂ interacting with NOTT-300(Cr) material; however, this technique may be able to offer insight into some of the differences between the Cr and Al systems. As the electronic properties and effective nuclear charge of Cr(III) are different to those of Al(III), the properties of the bridging –OH group in these frameworks are likely to be different, for example in terms of pK_a values for the OH group. It is expected that the interaction between CO₂ and the bridging –OH will also differ.

A sample of NOTT-300(Cr) was activated at 110 °C under vacuum to remove all solvent molecules in the pores. The PXRD pattern for desolvated NOTT-300(Cr) was collected and complete activation was confirmed by the structural refinement (Fig. 2.21 and 2.22). The sample was then dosed with 1 bar CO₂ and allowed time (~1 hr) to equilibrate before a pattern for the CO₂-loaded material was collected.

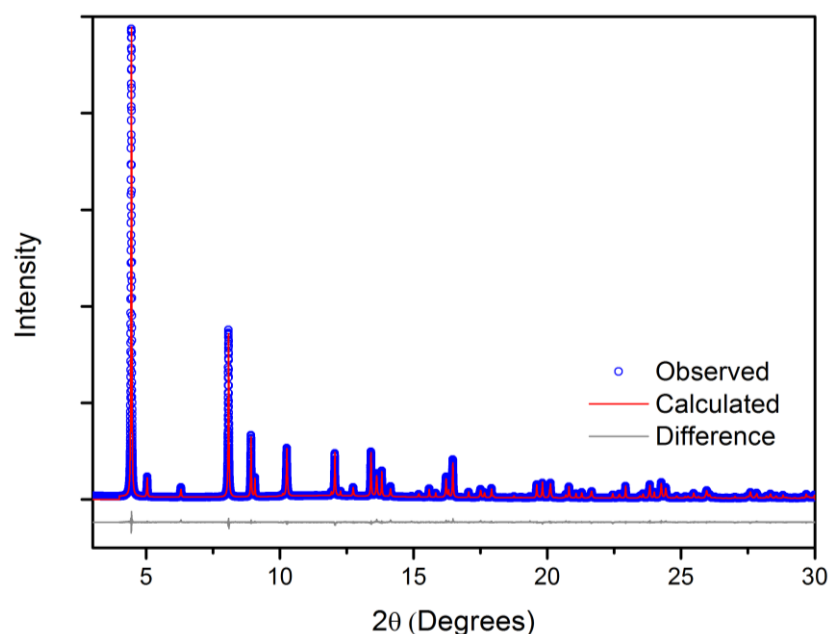
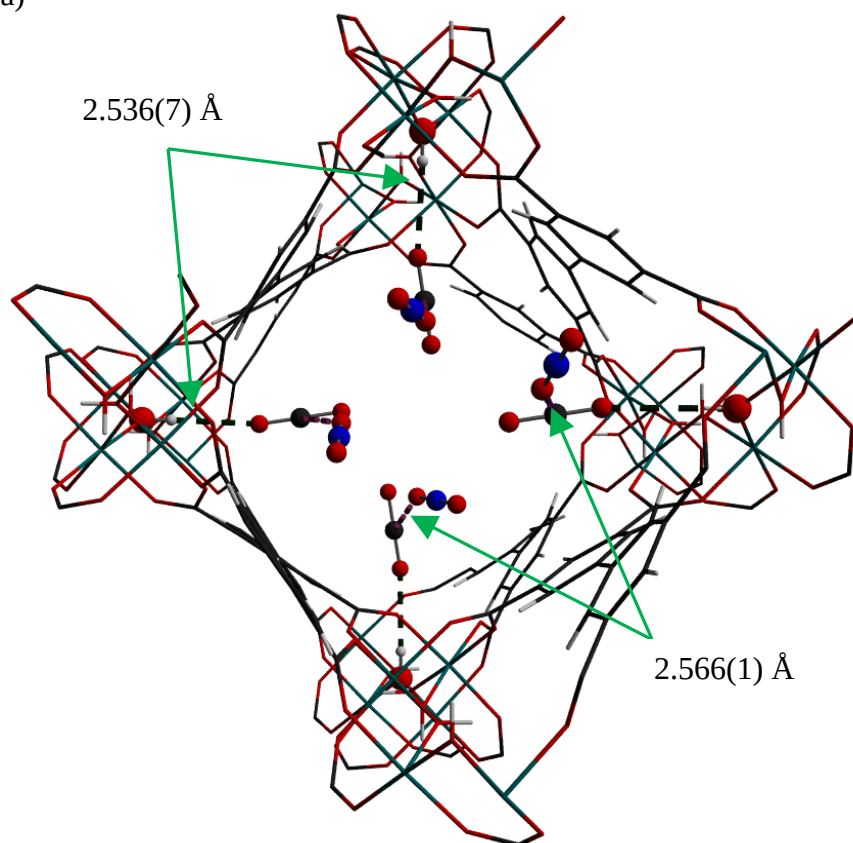


Fig. 2.21 PXR D patterns [observed (blue), calculated (red) and difference (grey)] for the Rietveld refinement of CO₂ loaded NOTT-300(Cr), λ - 0.825633.

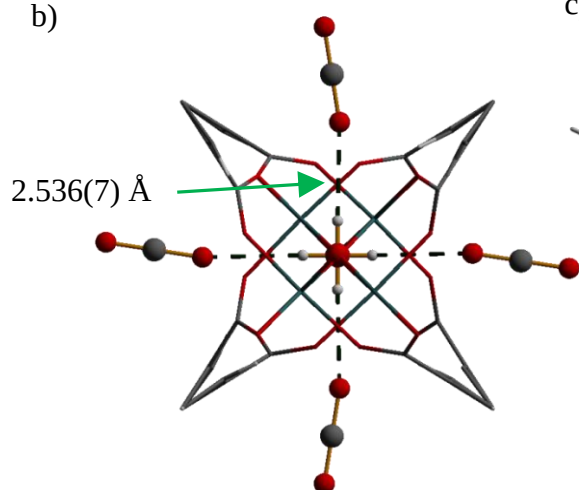
It was found that there are two distinct CO₂ binding sites within the CO₂ loaded-NOTT-300(Cr) complex, CO₂(I) and CO₂(II) (Fig. 2.22). CO₂(I) interacts with the bridging –OH group of the framework in an almost end-on fashion with a OH⋯OCO distance of 2.536(7) Å, the interaction is not fully linear with a bend in the –O-H---O interaction of 160 °. Due to this slightly bent interaction the CO₂(I) molecules are closer to the aromatic protons on the phenyl ring of the ligand, providing further supportive interactions (CH⋯OCO distances ranging from 2.927(4)-3.986(8) Å). The CO₂ molecules exhibit positional disorder, as the ideal position is to the side of the -OH and therefore can be located either side of the -OH group. As such the maximum occupancy for each site is 0.5, which is equivalent to one CO₂ per -OH group which is consistent with the adsorption at 1 bar. The disorder is removed from the structural figures for clarity. CO₂(II) interacts predominantly with CO₂(I) and

the position of CO₂(II) is reinforced by collective weak interactions from aromatic protons. CO₂(II) interacts with CO₂(I) in a bent T-shape, with a CO₂(I) – CO₂(II) (O=C=O $\cdots$ CO₂) distance of 3.566(1) Å. The differences between NOTT-300(Al) and NOTT-300(Cr) help to explain the differences in uptakes at high and low pressures, and also help clarify the differences observed in the heat of adsorption calculations. At low pressures the dominant behaviour in adsorption is between the framework and CO₂ and as the pressure increases and all CO₂(I) sites become occupied, the interactions between CO₂(I) and CO₂(II) become the dominant factor in adsorption. In NOTT-300(Al) the –OH $\cdots$ OCO(I) distance is 2.33Å, shorter than that found in NOTT-300(Cr) by 0.2 Å, indicating the interaction is stronger in the Al(III) material, consistent with the higher heat of adsorption and also the higher uptakes below 0.2 bar. However, the CO₂(I)-CO₂(II) distance (O=C=O $\cdots$ CO₂ - 3.92 Å) observed is longer than that for NOTT-300(Cr) indicating the dipole interactions between the CO₂ molecules is stronger in NOTT-300(Cr). The overall increased uptake of CO₂ by NOTT-300(Cr) can thus be attributed to both an increase in size of the pores, allowing increased available space, and also the strong interaction between CO₂(I) and CO₂(II) as both play dominant roles in uptake at higher pressures and loadings.

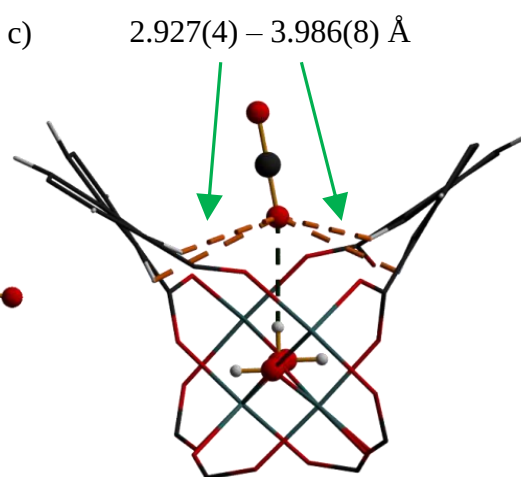
a)



b)



c)



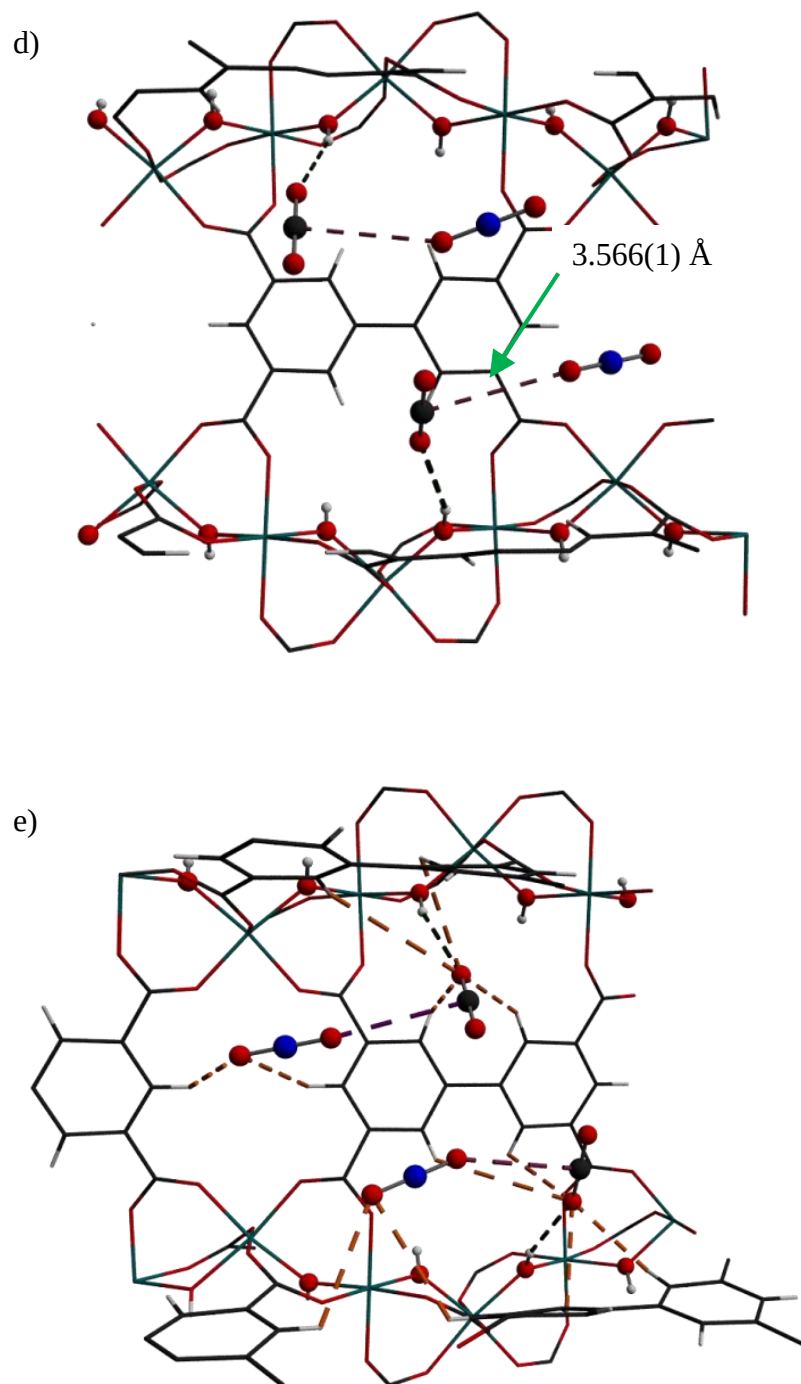


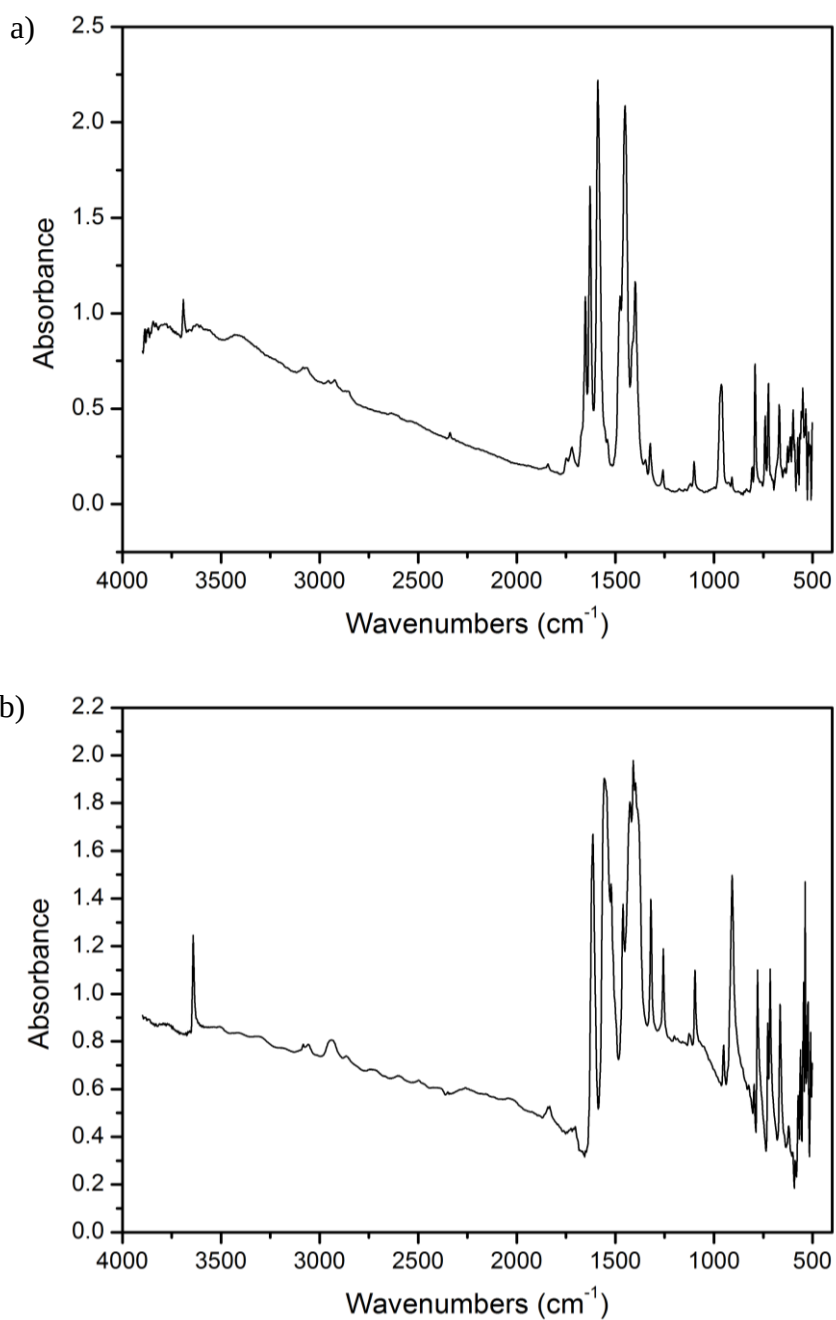
Fig. 2.22 Views of the structure of CO₂ loaded NOTT-300(Cr) obtained from PXRD with positional disorder removed for clarity. (Cr – teal, oxygen – red, carbon – grey, hydrogen – white). **a)** View of adsorbed CO₂ in the pore channel. The adsorbed CO₂ molecules and μ_2 -OH groups are highlighted in ball and stick mode. The carbon atom of CO₂ (II) is highlighted in blue. The H-bonds between O(δ^-) of CO₂ and H(δ^+) from the -OH group is highlighted in green,

[O $\cdots$ H = 2.53 Å], dipole interactions between CO₂ (I) and (II) are highlighted in purple [O=C=O $\cdots$ CO₂ = 3.56 Å] and van der Waals interactions between aromatic hydrogens and CO₂ (I) and (II) are highlighted in orange [O $\cdots$ H = 2.9 – 3.9 Å]. **b)** Detailed view of O-H $\cdots$ OCO H-bonds and the bent angle of interaction, the <OCO bond angle is 160°. **c)** View of cooperative/assistive van der Waals interactions between aromatic hydrogens and CO₂ (I). **d)** CO₂ (I) and CO₂ (II) dipole interaction and packing in the channel. **e)** Detailed view of CO₂ (I) and CO₂ (II) dipole interaction and additional van der Waals interactions between adsorbed gas and framework (distances not included for clarity). The C-O bond distances in CO₂ are 1.18 (CO₂(I)) and 1.14 Å (CO₂(II)).

2.2.9 *In Situ* IR Studies of Bare and CO₂ Loaded NOTT-300(Al) and NOTT-300(Cr)

To probe further the binding interaction between the adsorbed CO₂ molecules and the framework, a series of *in situ* IR experiments were carried out at Diamond Light Source using an environmentally controlled cell on an IR microscope, using synchrotron light as an intense IR source. Both NOTT-300(Cr) and NOTT-300(Al) were studied at varying concentrations of CO₂ in He. Monitoring how the IR absorption of the –OH group shifts with the different CO₂ concentrations allows us to monitor how the O=C=O $\cdots$ HO interaction changes with increasing CO₂. To be able to observe the position of the ν (OH) stretch in the bare MOF, the sample was activated in the cell at 373 K under vacuum to remove all residual water from the pores, which overlaps significantly with the ν (OH) stretch region of the spectrum. Initial spectra were then recorded with a continuous flow of He through the cell. Using a continuous flow kept the total cell pressure at $\sim$ 1 bar, the percentage of CO₂ in the He flow was increased step wise to achieve a range of partial pressures of CO₂ from 0 to 1 bar. Therefore in this section, references to CO₂ as x % equate to partial

pressures of CO₂ of x/100 bar. *In situ* IR experiments provide the possibility of monitoring the change of the $\nu(\text{OH})$ stretching vibration as a function of increasing CO₂ loading for both systems and thus provides insight into how the Cr(III) and Al(III) differ, especially at lower pressures when the most favourable binding sites are involved.



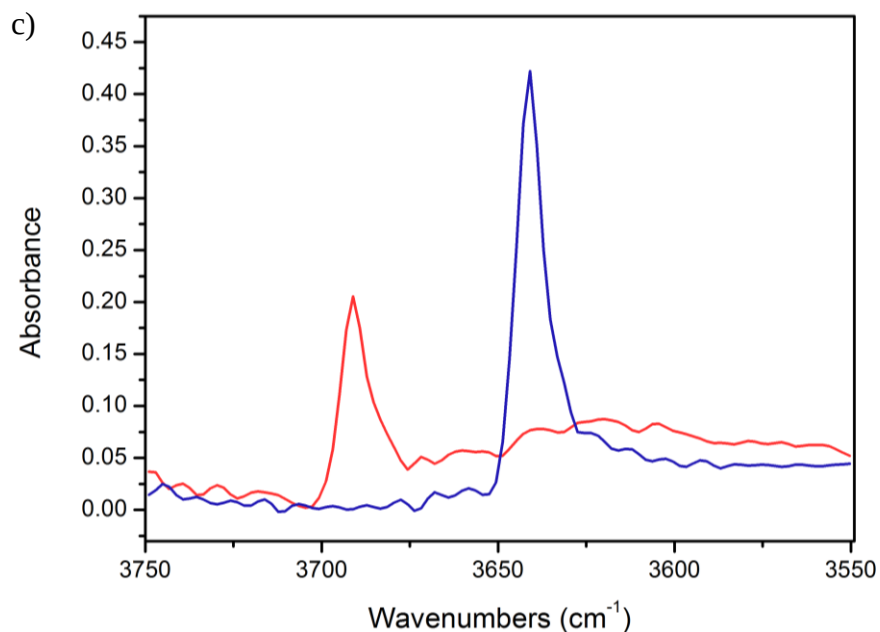


Fig. 2.23 **a)** IR spectrum of activated NOTT-300(Al), **b)** IR spectrum of activated NOTT-300(Cr), **c)** $\nu(\text{OH})$ region of the IR spectra of activated NOTT-300(Cr) (blue) and NOTT-300(Al) (red).

There is a clear difference in the observed position for the $\nu(\text{OH})$ stretch between the two samples that demonstrates that the metal centre present in the framework affects the properties of the $-\text{OH}$ group (Fig. 2.23c). The $\nu(\text{OH})$ stretch observed for NOTT-300(Al) is at higher energy (3691 cm^{-1}) compared with NOTT-300(Cr) (3641 cm^{-1}). Al(III) has a higher effective nuclear charge than Cr(III), and will electrostatically pull electron density from $\delta^- \text{O}$ in the OH moiety towards itself. This in turn creates a more δ^+ environment at the H, which we predicted would afford stronger H-bonds.

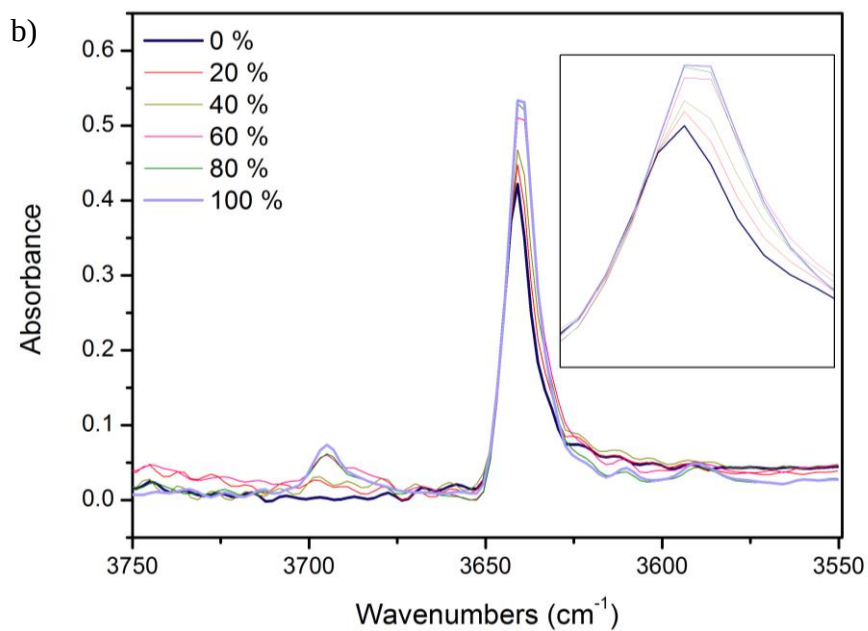
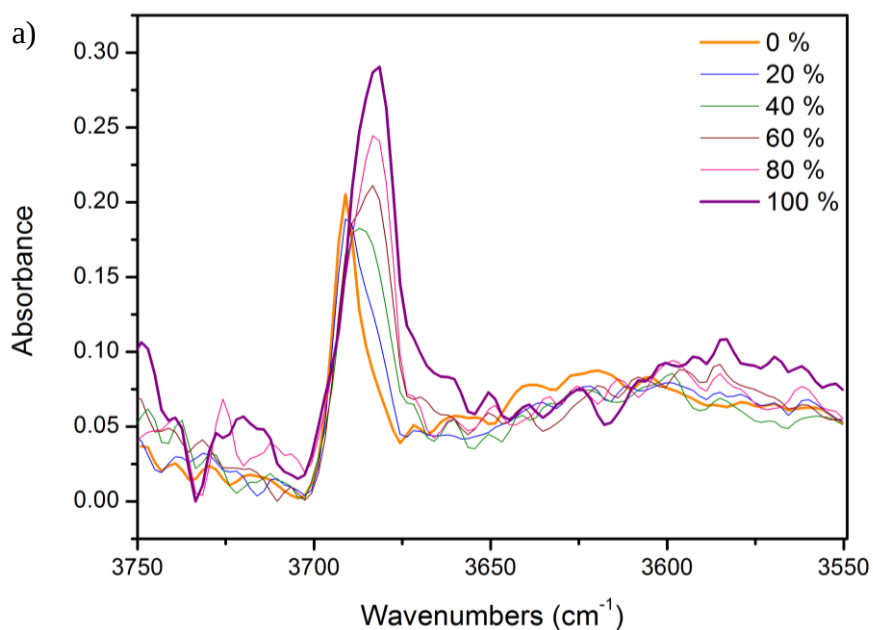


Fig. 2.24 IR spectra showing $\nu(\text{OH})$ stretch region of **a)** NOTT-300(Al) and **b)** NOTT-300(Cr) as the CO_2 concentration increases from 0 $\rightarrow$ 100%.

For NOTT-300(Al) the position of $\nu(\text{OH})$ shifts to lower energy upon introduction of CO_2 into the system by 8 cm^{-1} , from $3691 - 3683\text{ cm}^{-1}$, indicating a weakening of the O-H bond as H-bonds are formed with CO_2 (Fig. 2.24a). This is not as pronounced in the spectra recorded for NOTT-300(Cr) as the position

of the $\nu(\text{OH})$ band only shifts a small amount ($\sim 1 \text{ cm}^{-1}$, $3641 - 3640 \text{ cm}^{-1}$) (Fig. 2.24b). This is consistent with the interactions between CO_2 and the framework being weaker when Cr(III) is the metal centre than in NOTT-300(Al). This difference in H-bond strength is in good agreement with the *in situ* CO_2 loaded PXRD data, which shows a longer distance ($2.54 \text{ \AA}$ vs. $2.34 \text{ \AA}$) between the -OH group and CO_2 molecules in NOTT-300(Cr) than NOTT-300(Al).

CO_2 also has IR vibrations in this region, typically at ~ 3700 and 3600 cm^{-1} .⁴⁶ The NOTT-300(Cr) spectrum displays new bands at 3694 cm^{-1} and 3590 cm^{-1} above CO_2 concentrations of 60%. These peaks grow with increasing CO_2 concentration (after the gaseous CO_2 spectrum has been subtracted) and are hence assigned to “bound” CO_2 . Similar peaks have been observed in other examples of CO_2 bound in MOFs in the literature.⁴⁷

	$\nu(\text{OH})$ (cm^{-1})	$\nu(\text{OH})$ (OH+ CO_2) (cm^{-1})	CO_2 combination bands (cm^{-1})
NOTT-300(Cr)	3640.7	3640.0	3694.9 3589.7
NOTT-300(Al)	3690.6	3683.2	3590.5

Table 2.7 Peak positions of $\nu(\text{OH})$ stretch and CO_2 combination bands present in IR spectra of NOTT-300(Al) and NOTT-300(Cr).

We can therefore monitor the disappearance of -OH in bare-MOF and the appearance of -OH+ CO_2 as a function of CO_2 concentration and time. This allows us an insight into the kinetics and uptake of CO_2 adsorption in these materials. Measurements were performed in the same manner for both NOTT-300(Al) and NOTT-300(Cr). Repeated spectra were taken at constant time intervals for each stepwise partial pressure increase of CO_2 (*i.e.* $0 \rightarrow 20\%$, $20 \rightarrow 40\%$ *etc.*) until each step had equilibrated. Once the spectra ceased changing, *i.e.* the internal gas loading of the MOF had equilibrated, the gas

mixture was increased to the next partial pressure step and the measurement repeated. As a general observation for each pressure step the equilibration process is significantly slower for NOTT-300(Al) than for NOTT-300(Cr), an example of this is shown in Fig. 2.25.

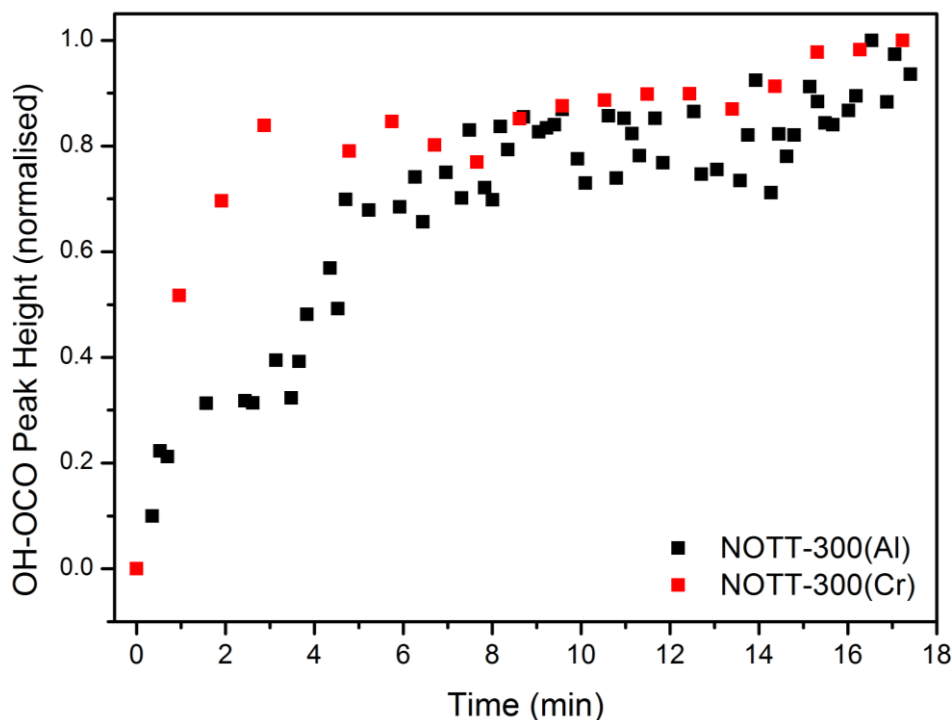


Fig. 2.25 Peak height of the $\nu(\text{OH})$ stretch corresponding to the $-\text{OH}+\text{CO}_2$ species (normalised to the highest value) for both NOTT-300(Al) and NOTT-300(Cr) vs. time after increase in CO_2 from 0 to 20 %.

There are likely two factors causing this effect, a) the reduction in pore size for NOTT-300(Al) ($\sim 6.5 \times 6.5 \text{ \AA}$ in NOTT-300(Al) and $\sim 6.8 \times 6.8 \text{ \AA}$ in NOTT-300(Cr)) which may reduce the mobility of the CO_2 in the pore, and b) the difference in strength of the H-bonds formed between the CO_2 molecules and the $-\text{OH}$ group of the two frameworks affects the transport mechanism of CO_2 along the channel.

Figure 2.26 shows the time dependant behaviour of the $\nu(\text{OH})$ groups in both MOFs (peak height plotted as a % of its maximum value) across the whole pressure range as the pressure was increased in 0.2 bar ppCO_2 increments up to 1 bar. Figure 2.26a shows clearly for NOTT-300(Al) there is a slow change in the loss of the peak corresponding to the 'bare-OH' on the time scale of each step (approx. 15-20 mins per step) and the corresponding behaviour is seen for the growth of the CO_2 -bound '-OH+ CO_2 ' peak. Given the shape of the graph, equilibration at each partial pressure may not have been fully achieved before the next step was made, particularly at the higher ppCO_2 steps.

The same experiment for NOTT-300(Cr) (Fig. 2.26b), has quite a different profile. The loss of 'bare-OH' and the growth of '-OH+ CO_2 ' are well matched and for each step show a rapid period of adjustment before reaching a plateau in advance of the next change in pressure (*e.g.* within 5 minutes for the first 0 - 20 % CO_2 step). This is consistent with much faster transport of CO_2 into the framework in NOTT-300(Cr) than in NOTT-300(Al). Notable, the equilibration of the peak heights appears to take longer at higher partial pressure steps, which would be consistent with the gradual blocking of existing binding sites by CO_2 already in the pores. Although the noise in the peak height profile at these higher percentages of CO_2 make this a purely qualitative observation.

It was shown in MOF-74, a channel-containing MOF with open metal sites, that there was a short hopping pathway as CO_2 molecules hopped from one open metal site to the next.⁴⁸ While the H-bond in NOTT-300(M) is weaker than CO_2 interactions with open metal sites in MOF-74, it clearly still plays a significant role in transport of CO_2 in the MOF structure. A combination of weaker H-bonds

and faster uptake kinetics is therefore consistent with an enhancement of a hopping style mechanism. There are further experiments and computational methods that could be used to further investigate the transport of CO₂, however, they are beyond the scope of this work.

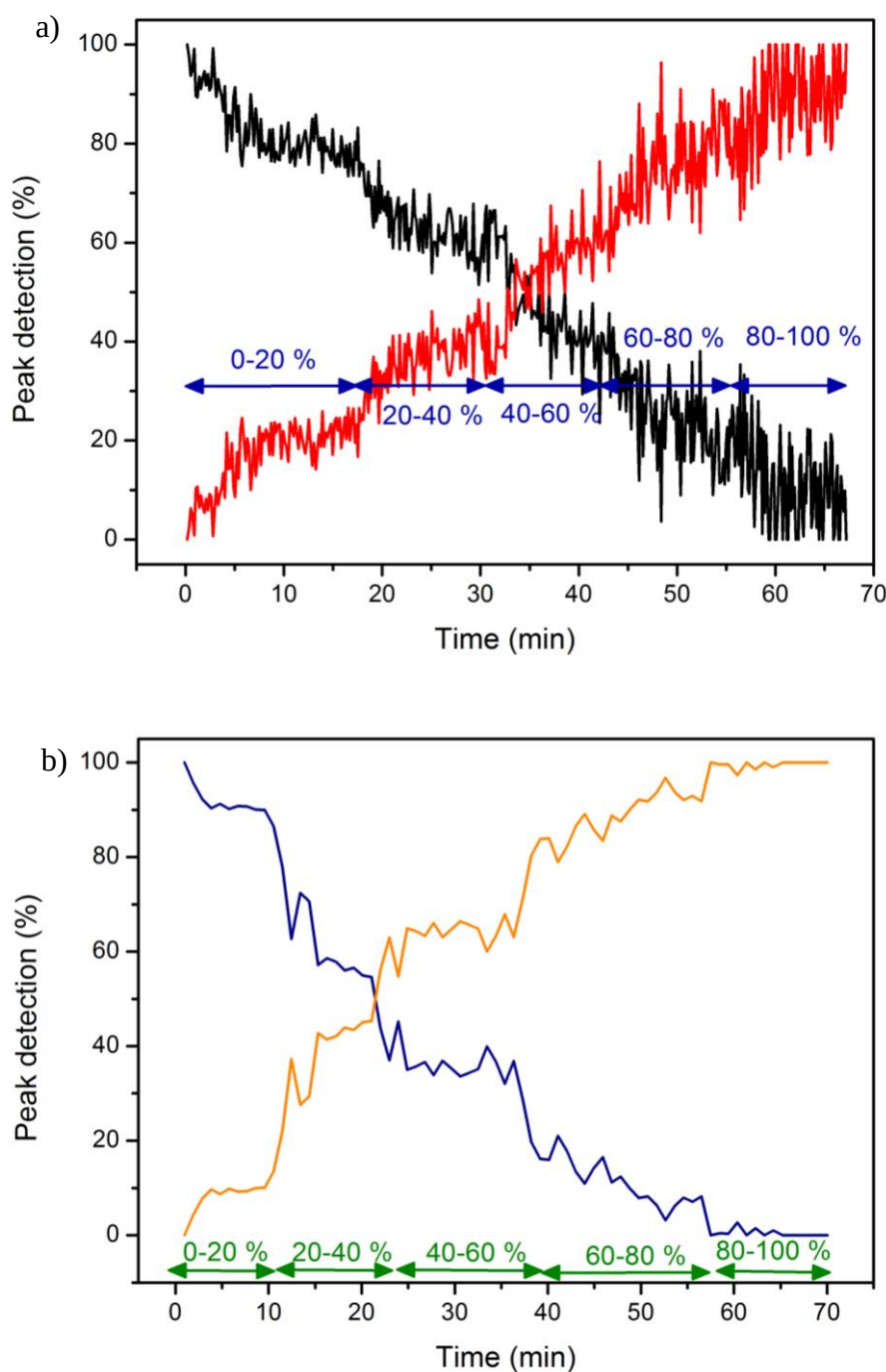


Fig. 2.26 % of $\nu(\text{OH})$ and $\nu(\text{OH})\text{-OCO}$ peak detection as a function of time and CO₂

concentration showing the differences in equilibration time for **a)** NOTT-300(Al) (black – bare OH, red - OH-OCO) **b)** NOTT-300(Cr) (orange – bare OH, blue – OH-OCO).

2.2.10 Separation from CO₂/N₂ in NOTT-300(Al) by Breakthrough Experiments

To further assess the performance of NOTT-300(Al) in CO₂ separation processes, breakthrough experiments were performed wherein a mixture of CO₂ and N₂ is flowed over a fixed bed of NOTT-300(Al) and the exiting gas stream is then analysed by mass spectrometry. The time taken from introduction into the system until detection of a gas is the “breakthrough” time; a longer breakthrough time means high adsorption capacity and affinity of the gas to the porous material. Before the experiment was conducted the sample of NOTT-300(Al) was heated to 100 °C under a flow of He to fully activate the sample. Once activation was complete, a flow of N₂ and CO₂ was introduced to the environment and the time taken for the gas to travel through the sample was recorded. Two different experiments were undertaken with differing ratios of CO₂/N₂, 1:1 and 1:9.

The first experiment consisted of a mixed N₂/CO₂ stream of 1:1 at a flow of 2 ml min⁻¹ each (Fig. 2.27a). The breakthrough plot clearly shows N₂ eluting from the system very quickly, as no interactions are formed between the N₂ and the framework, allowing the gas to flow freely through the sample. There is a small amount of CO₂ detected (15 %) at ~ 20 mins, this is due to poor sample packing and the CO₂ travelling through gaps between crystallites as opposed to through the porous material itself. This can be reduced by repacking the sample with

greater pressure. This low level of CO₂ remains almost constant until the sample reaches saturation and the “true” CO₂ breakthrough is achieved at 80 mins. It takes a further 100 mins for the concentrations of the exhaust gas to equal the concentration of the inlet gas. There is good separation of the gases achieved by this material at relatively high partial pressures of CO₂.

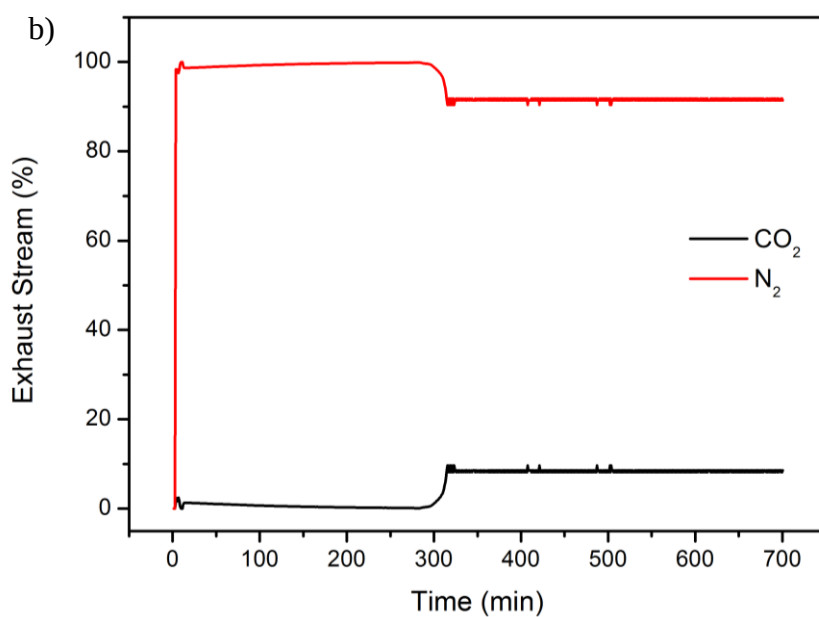
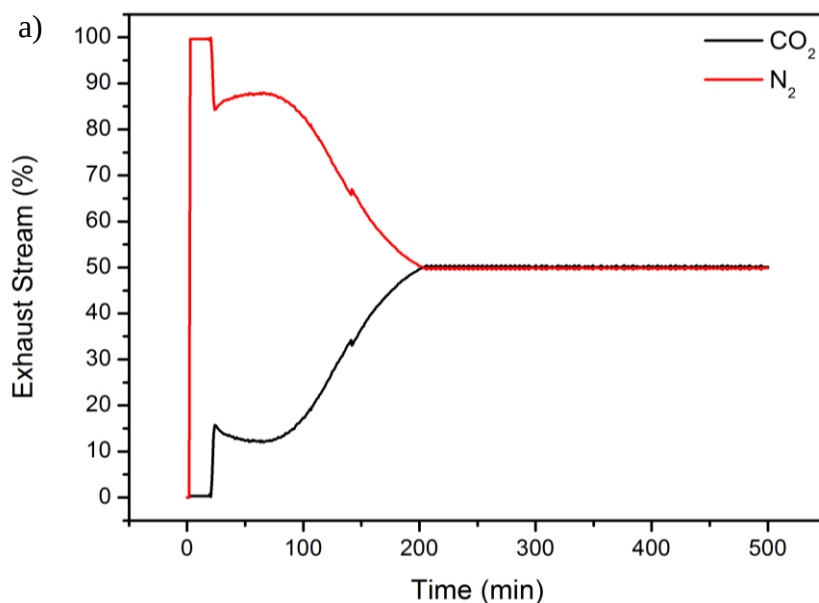
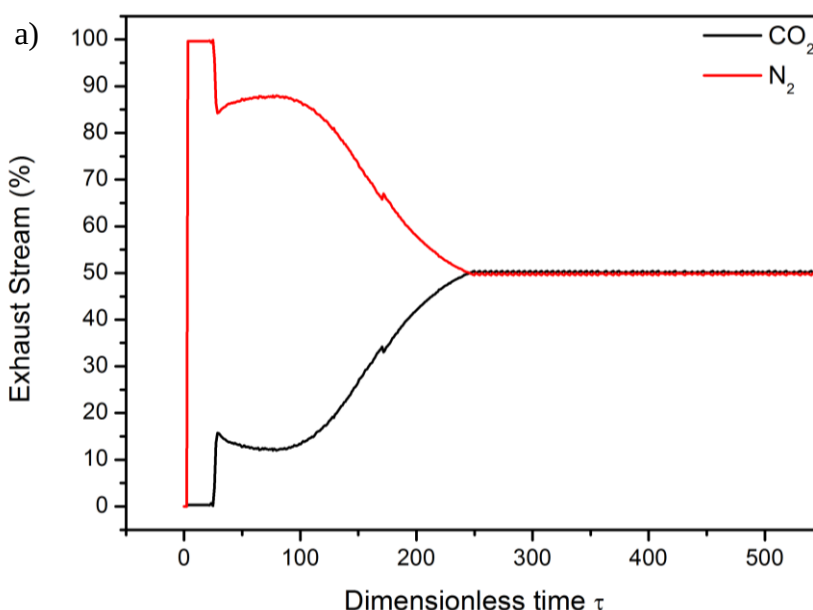


Fig. 2.27 Breakthrough curves for NOTT-300(Al) for **a)** 1:1 CO₂/N₂ and **b)** 1:9 CO₂/N₂.

A second breakthrough experiment was performed with a much lower concentration of CO₂ (10 %) in order to assess the CO₂ separation capability of this material at low partial pressures. It is this region that is of interest for post-combustion carbon capture. CO₂ uptake at these low pressures is often low, and many groups are investigating ways to increase the uptakes in this low pressure region.^{49,50} Isotherm data for NOTT-300(Al) displays good uptake of CO₂ at these lower pressure regions. However, it is not known if or how the high concentration of N₂ in the gas stream will affect CO₂ uptake. The breakthrough curve obtained shows almost instantaneous breakthrough and detection of N₂, and the time taken for the sample to reach CO₂ saturation and therefore for the CO₂ to breakthrough is much longer than for the 1:1 mixture (Fig 2.27). CO₂ is not detected until ~ 300 mins, clearly demonstrating the capability of NOTT-300(Al) to separate CO₂ from a 1:9 CO₂:N₂ mixture. NOTT-300(Al) clearly displays a high affinity for CO₂ and the presence of N₂ does not hinder this.



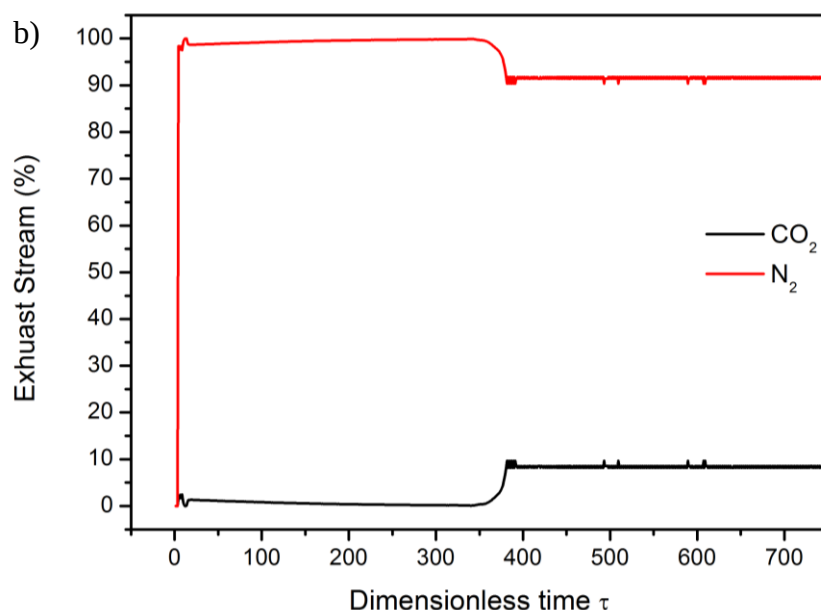


Fig. 2.28 Breakthrough curves in dimensionless time for NOTT-300(Al) for **a)** 1:1 CO₂/N₂ and **b)** 1:9 CO₂/N₂.

Even after conversion to dimensionless time (Fig. 2.28), the difference in breakthrough of the two gases is large; indicating the good separation of CO₂ and N₂ is due to the material and not the length of the column.

2.2.11 CO and N₂ uptakes in NOTT-300(Cr)

The separation of CO from CO:N₂ gas streams is of importance as CO is a commonly used resource for carbon based chemical products.⁴⁵ The large amount of CO produced by industrial processes is mixed with other gases, often N₂, and therefore cannot be used in the production of carbon based products. This waste mixture of gases is then burned to generate CO₂ which is less toxic but has its own detrimental environmental effects.⁵¹ The separation of these gases, however, is known to be difficult since the physical properties of CO and N₂ are very similar (Table 2.8).

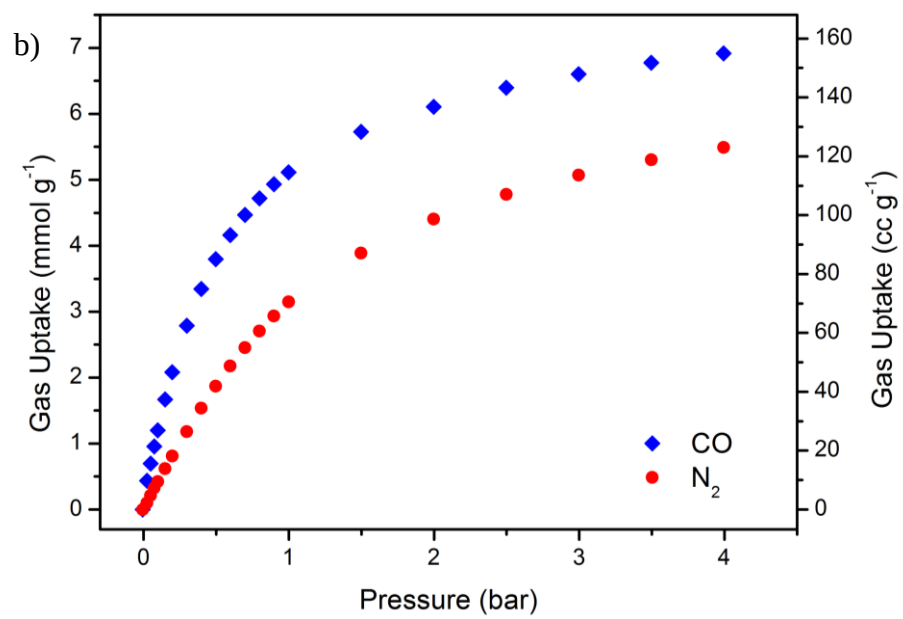
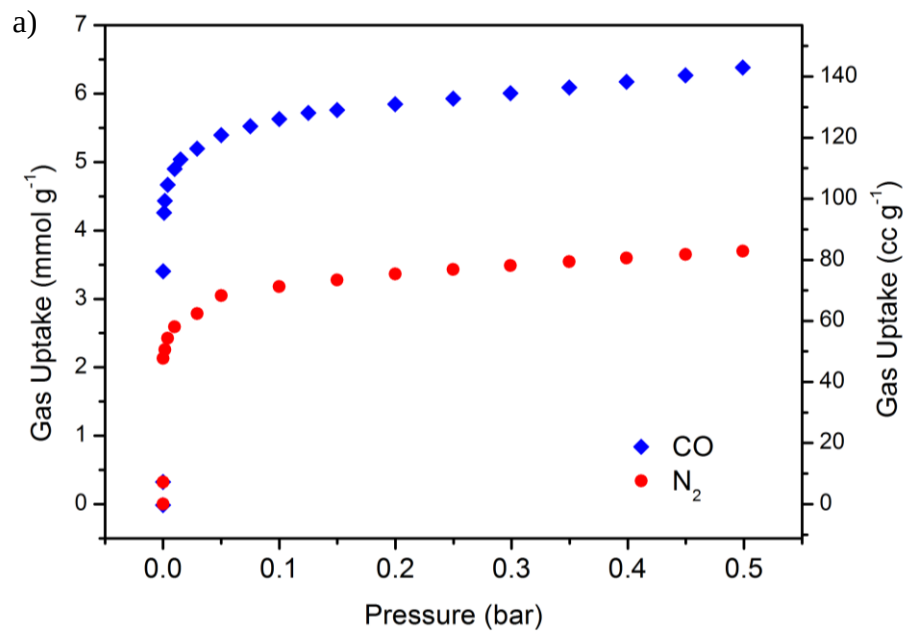
	CO	N ₂
Kinetic diameter Å	3.76	3.64
Number of electrons	14	14
Standard boiling point K	81.7	77.4
Critical temperature K	132.9	126.2
Critical pressure atm	34.5	33.5

Table 2.8 Physical properties of CO and N₂.

There are few reported examples of MOFs displaying CO selectivity versus N₂, as the gases have very similar properties the uptakes tend to also be similar. A recently published example of a MOF material with the ability to selectively adsorb CO from a CO/N₂ mixture is [Cu(aip)(H₂O)] (aip – 5-azidoisophthalate), a Cu(II) MOF reported by Kitagawa *et al.*⁵² The framework consists of Cu(II) paddlewheel units that have an open coordination site after activation. It was found that CO binds to the Cu(II) paddlewheel which leads to a local structural re-arrangement and opening an otherwise inaccessible channel thus enhancing adsorption of CO. This channel remains inaccessible to N₂ and this process was termed “self-accelerated adsorption”. The adsorption of CO and N₂ was recorded at 120 K up to 1 bar and reached 8.06 mmol g⁻¹ and 3.17 mmol g⁻¹, respectively. The calculated IAST CO/N₂ selectivity at 120 K is 5.

When measuring the adsorption of N₂ and CO in NOTT-300(Cr) for the purpose of CO₂ selectivity calculations, a difference in adsorption uptakes was observed and investigated further to assess possible CO versus N₂ selectivity. Adsorption isotherms were carried out for N₂ and CO under a variety of conditions, 77 K (1 and 0.5 bar, respectively), 195 K (4 bar), 223 K, 273 K and 293 K (all at 5 bar) in order to assess the differences in uptake and the possibility of separation, a summary of CO and N₂ uptakes is shown in Table 2.9.

The isotherms measured at 77 K display very rapid uptakes for both CO and N₂, with a large amount of the adsorption occurring below 0.05 bar (CO, 5.39 mmol g⁻¹, N₂, 3.04 mmol g⁻¹) (Fig. 2.29a). At 0.5 bar NOTT-300(Cr) reaches a maximum CO adsorption of 6.18 mmol g⁻¹, with N₂ reaching 3.69 mmol g⁻¹ under the same conditions. The highest CO uptake for this material was recorded at 195 K and 4 bar and reached a total of 6.91 mmol g⁻¹; under these conditions N₂ adsorption reached a total of 5.49 mmol g⁻¹ (Fig. 2.29b). At all temperatures the uptakes recorded for CO were higher than those for N₂. This is a positive indication that NOTT-300(Cr) possesses the capability to separate CO from CO/N₂. However, the difference in uptakes and therefore the selectivity, decreases when the temperature is increased to more ambient temperatures (273 K, 293 K) which are the most important in terms of low energy CO separation. The highest calculated selectivity for this material was 3, at 195K. Although lower than that found for Kitigawa's MOF this was calculated from higher temperature data. It is possible the two materials will have comparable selectivities at the same temperature.



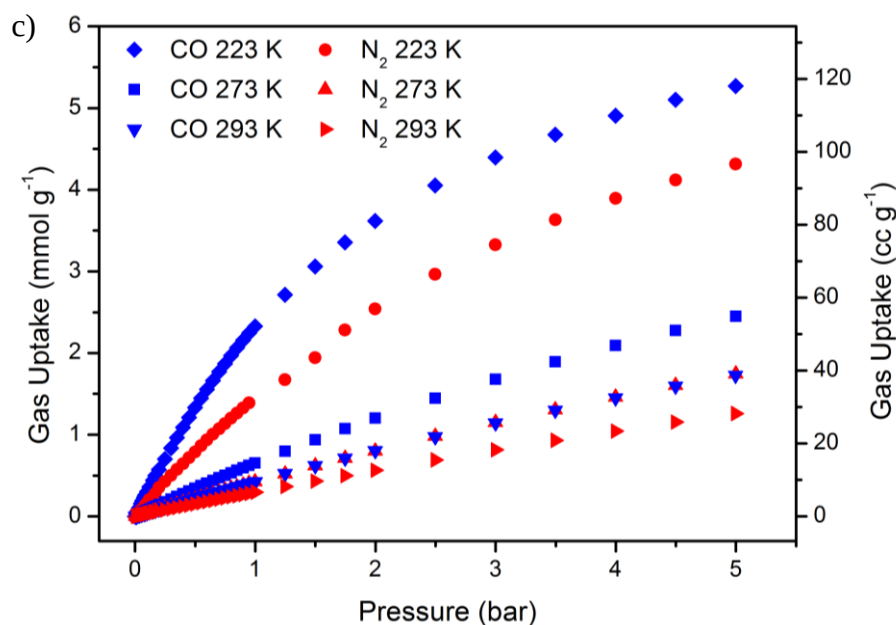


Fig. 2.29 CO (blue) and N₂ (red) adsorption isotherm for NOTT-300(Cr) recorded at **a)** 77 K and 0 – 0.5 bar **b)** 195 K and 0 – 4 bar and **c)** 223 K, 273 K and 293 K from 0 – 5 bar.

	CO (mmol g ⁻¹)	N ₂ (mmol g ⁻¹)
77 K	6.18	4.37
195 K	6.91	5.49
223 K	5.26	4.31
273 K	2.45	1.74
293 K	1.73	1.26

Table 2.9 CO and N₂ adsorption uptakes for NOTT-300(Cr).

CO/N ₂	Ratio of isotherm slopes	IAST
195 K	2.5	3.0
223 K	1.8	2.0
273 K	1.6	1.8
293 K	1.4	1.5

Table 2.10 Calculated CO/N₂ selectivity for NOTT-300(Cr) from the experimental isotherms.

2.3 Conclusion and Future Work

In this chapter the synthesis of a Cr(III) containing MOF isostructural to NOTT-300(Al) has been discussed and the gas adsorption properties have been investigated in terms of CO₂ separation and storage. NOTT-300(Cr) displays high thermal stability as confirmed by TGA and variable temperature PXRD,

decomposing above 490 °C. The CO₂ adsorption capacity of this material was greater than that displayed by NOTT-300(Al), reaching 10.08 mmol g⁻¹ at 273 K and 20 bar. In fact NOTT-300(Cr) shows higher adsorption capacity for all gases recorded; however, this in turn leads to a decrease in CO₂ selectivity. It is clearly shown that a change in metal centre affects the gas adsorption properties of this framework material. This is because the dominant interaction in CO₂ adsorption is based upon H-bonding between the μ_2 -OH group, and the metal centres affect the chemistry (pKa) of this –OH group which is reflected in the binding properties of this group to CO₂. CO₂ loaded *in situ* PXRD experiments confirmed the presence of these interactions and also showed these interactions to be stronger in NOTT-300(Al), which are responsible for the higher CO₂ adsorption at low pressures (0-150 mbar). IR studies on CO₂ loaded materials also provided useful insights in to the behaviour of the –OH group as a function of CO₂ concentration with NOTT-300(Cr) showing faster CO₂ adsorption kinetics.

The CO₂ selectivity of NOTT-300(Al) was further investigated by carrying out breakthrough experiments in two different CO₂/N₂ concentrations. There was a large separation observed in both experiments. Of particular interest is the separation of CO₂ vs. N₂ in a 1:9 mixture which closely mimics the proportion of these gases in flue gas. This confirms the potential of NOTT-300(Al) for CO₂ capture in post combustion systems.

In the process of investigating CO₂ selectivity, it was found that NOTT-300(Cr) possesses CO vs. N₂ selectivity, especially at lower temperatures. This is rare in MOFs as both gases have similar properties.

There is significant potential for future work in this area such as dual component adsorption isotherms in the presence of water vapour with both NOTT-300(Cr) and NOTT-300(Al) as the CO₂ adsorption could be significantly affected by the presence of the water vapour. To further assess the CO₂ separation ability of NOTT-300(Cr), and to investigate how the faster kinetics affect the separation ability, breakthrough experiments could be performed. Further investigation into the possibility of CO/N₂ separation, (lower temperature isotherms, dual component adsorption and breakthrough experiments) could provide some interesting results.

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Chapter 3 – Heterometallic NOTT-300(AlCr) Series – Effects of the Ratio of Cation Content on CO₂ Adsorption and Selectivity

3.1 Introduction

The concept of hetero-metallic MOFs is relatively new, with few deliberate examples in the literature. Most of these examples involve the presence of two or more metals with different oxidation states and/or coordination environments.^{1,2,3,4} There are several reasons for incorporating metals with different oxidation states such as increasing “guest-host” interactions, introducing a possible catalytic site within the framework and to control the framework structure/topology.^{5,6,7,8} The inclusion of different metals can be controlled by using ligands with multiple functional groups/donor atoms for coordination to different metals.^{9,10,11}

Dehnen *et al* recently reported the synthesis of a mixed metal MOF using a multifunctional ligand, 2-pyrazinecarboxylic acid (pcaH), to utilise the hard/soft binding nature of ligands/metals.¹² $[\text{Fe}_2\text{Ag}_2(\text{pca})_4(\text{pcaH})(\text{MeOH})_2](\text{ClO}_4)_2$ was synthesised from $\text{Fe}(\text{ClO}_4)_2$, $\text{Ag}(\text{NO}_3)$ and pcaH in MeOH and the structure was solved by single crystal X-ray diffraction (Fig. 3.1). The asymmetric unit consists of two Fe, two Ag and five ligands, one of which remains protonated. Both Fe^{2+} sites are 6-coordinate and have distorted octahedral geometries. Each Fe is coordinated to two N atoms and three O atoms from the ligand, and to a further O atom from MeOH. The coordinated MeOH can be removed upon activation leading to a coordinatively unsaturated Fe centre available for interaction with guest species. There are two distinct Ag sites within the framework, Ag(a) and Ag(b). Ag(a) is 5 coordinate and adopts a distorted trigonal bipyramidal geometry, coordinating to three N's (equatorial) and two O's (axial) from the ligand. The second Ag site, Ag(b), is tetrahedral and coordinates to three N atoms and one O atom provided by the ligand.

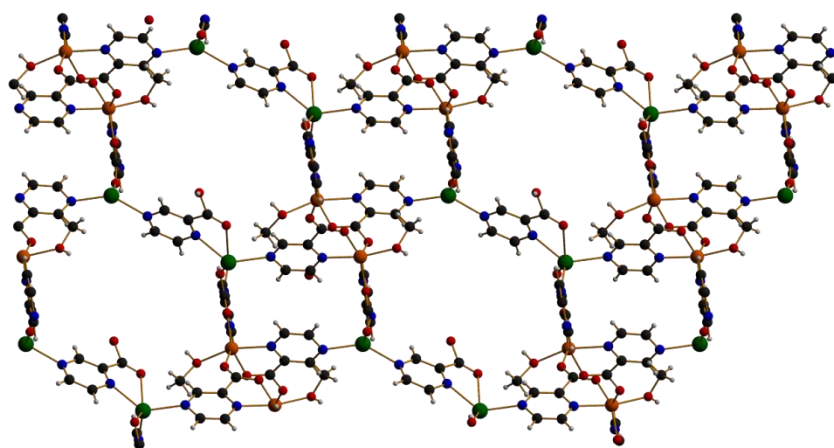


Fig. 3.1 View of the structure of $[\text{Fe}_2\text{Ag}_2(\text{pca})_4(\text{pcaH})(\text{MeOH})_2](\text{ClO}_4)_2$ along the b axis.¹²

The ligand adopts three types of coordination mode within the structure shown in Fig. 3.2. It is the presence of modes 2 and 3 which make this material a true bimetallic MOF as they connect the two different metals, creating homogeneity throughout the sample. The Lewis acid site at Fe, generated by removal of MeOH at temperature, is a possible site for catalysis and the catalysis of cyanohydrin formation from two aldehydes was tested. A conversion of 51% after 3 hours was observed with benzaldehyde, but the larger aldehyde (2-naphthaldehyde) had a much lower conversion, 9%, due to more limited access to the Fe sites.

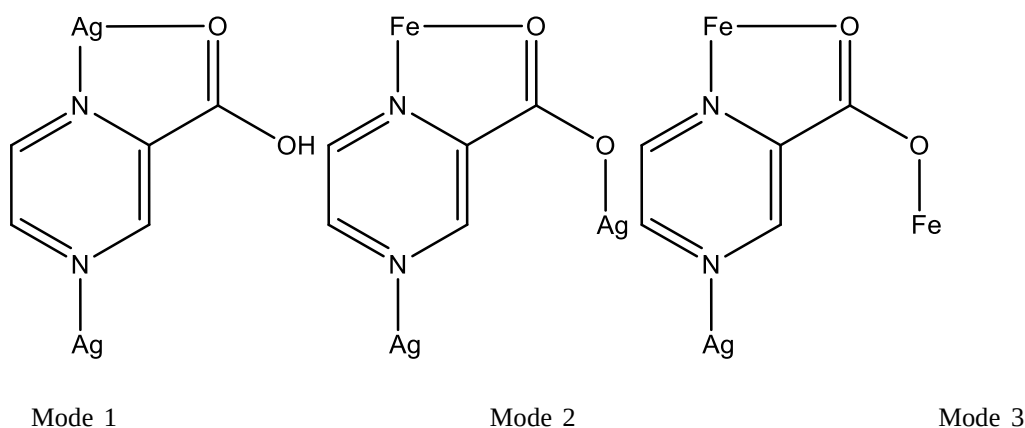
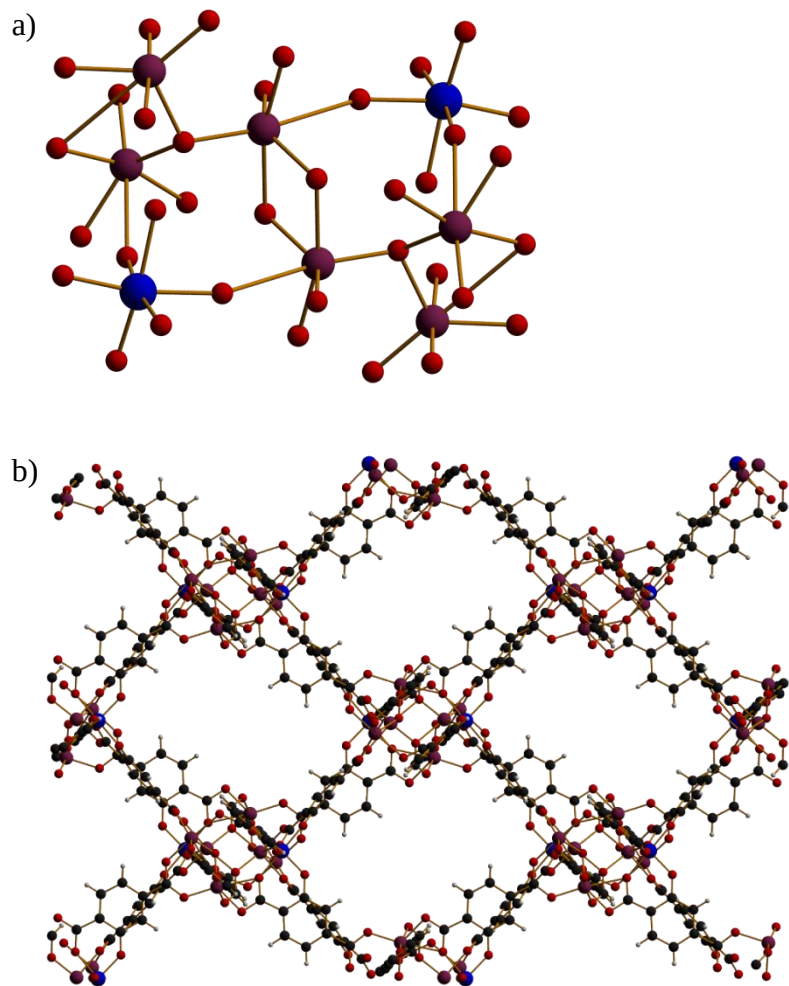


Fig. 3.2 Different binding modes of the ligand present within the MOF structure, showing the connection of the metal centres.¹²

The generation of mixed metal MOFs also provides a useful approach to the incorporation of otherwise difficult to use metals.¹³ For example, Yaghi *et al.* reported the inclusion of up to ten different metals in a mixed MOF-74 structure, for some of which the parent MOF structure is unknown.¹⁴ There has been a little work recently published on MOFs generated from high valent metals, as opposed to the more common M(II) that is used in the majority of MOF examples. The drawbacks associated with M(II) MOFs have been previously highlighted, particularly the instability in the presence of water. MOFs consisting of Ti^{4+} and Zr^{4+} have been reported to be hydrostable, however, there are limited examples in the literature due to the difficulty of their syntheses.¹⁵ The incorporation of these high valent metals into mixed metal MOFs could provide an easier synthetic route to desired hydrostable materials.^{16,5} An example of a mixed metal MOF containing a high valent metal centre (Ti^{4+}) has recently been reported by Chun *et al.* known as ZTOF-1 ($[\text{H}_2\text{N}(\text{CH}_3)_2][\text{Zn}_3(\text{OH})\text{Ti}(\text{obdc})_3(\text{HCO}_2)]$).¹⁷ This material consists of clusters of six Zn(II) and two Ti(IV) ions throughout the framework (Fig. 3.3) and was stable to activation. The MOF also displays

moderate thermal stability, decomposing at $\sim 250\text{ }^{\circ}\text{C}$, and reasonable CO_2 uptake, reaching 80 cc g^{-1} at 273 K and 1 bar (Fig. 3.3c).



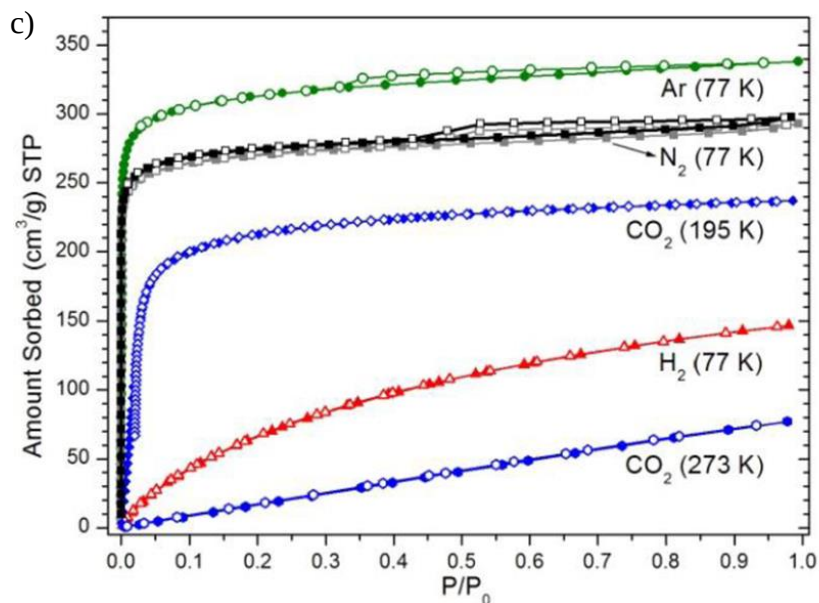
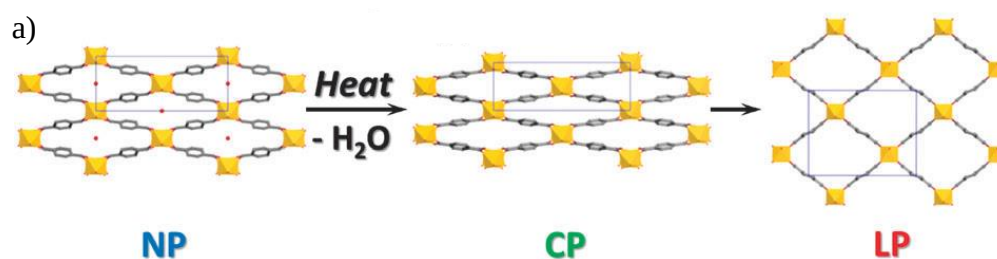


Fig. 3.3 a) View of Zn_6Ti_2 cluster found in ZTOF-1, **b)** View of ZTOF-1 along the a axis, **c)** Gas adsorption isotherms for ZTOF-1. Figures taken from reference 17.

There are even fewer reports of mixed metal MOFs that consist of crystallographically indistinguishable metal centres, possibly due to the fact that these particular systems offer none of the advantages described above for the mixed valent MOFs.^{18,19} However, substituting/doping of a second metal can still have large effects on the physical and mechanical properties of the framework.^{20,21,22} This is demonstrated by the control of the breathing behaviour of MIL-53 by varying/mixing the cations present as reported by Serre *et al.*²³ The heterometallic MIL-53(Cr/Fe) was synthesised and the breathing mechanism was investigated, as both the single metal MIL-53(Fe) and (Cr) display antagonistic breathing properties. The breathing of MIL-53 has been well studied, with many different metal centres used (Al, Cr, Ga, Fe *etc.*).²⁴ All MIL-53 materials were found to adopt the “narrow pore” (NP) form when solvated but can adopt either “large pore” (LP) or “closed pore” (CP) forms on removal of the solvent depending on the metal present within the framework.

MIL-53(Cr) achieves the LP form whereas MIL-53(Fe) adopts the CP form on desolvation. The mixed MOF, $\text{Cr}_{0.6}\text{Fe}_{0.4}(\text{OH})_{0.7}\text{F}_{0.3}(\text{BDC})$, exhibited significantly different breathing behaviour with a transition from NP form to CP form at ~ 350 K and a further transition to LP form at high temperatures, above 463 K. The adsorption properties of this mixed metal MOF also appeared to be different to both the single metal MOFs. CO_2 adsorption is a 2-step process in this framework, due to the structural transitions that occur as a function of loading/pressure from $\text{CP} \rightarrow \text{NP} \rightarrow \text{LP}$ (Fig. 3.4). The NP to LP transition occurs at ~ 10 bar in the CO_2 isotherm, higher than MIL-53(Cr) (2 bar) and lower than MIL-53(Fe) (> 20 bar). This leads to the conclusion that if the pore opening can be controlled, the uptakes and selectivity could feasibly be “tuned”.



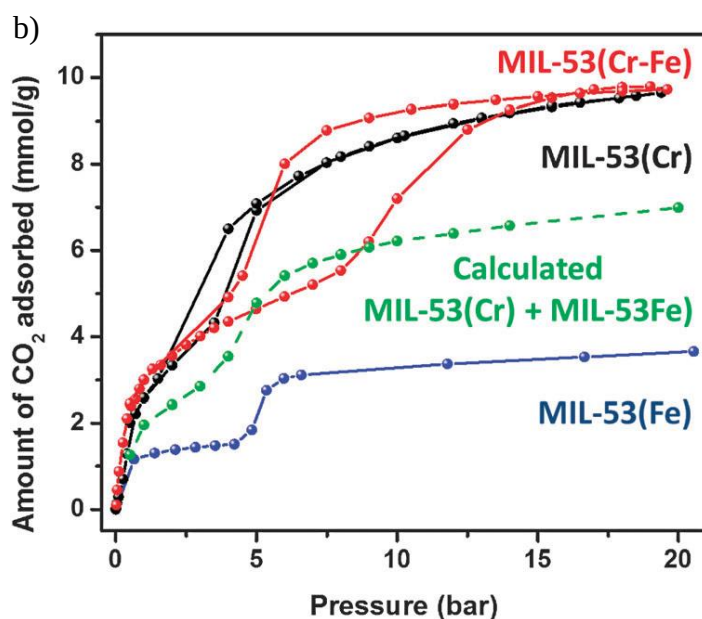


Fig. 3.4 a) A schematic of the breathing mechanism that occurs in MIL-53(Cr). **b)** CO₂ adsorption isotherm recorded at 283 K. Figure taken from reference 23.

As well as altering the properties of the MOFs such as gas uptake and catalysis, the introduction of a second metal site can also improve the stability of a material. This was demonstrated by Zhang *et al.* who reported the synthesis of a Zn MOF, [H₂N(CH₃)₂]₂[Zn₉(μ₃-OH)₂(BTC)₆(DMPU)₃], which was unstable to activation and completely decomposed.²⁵ Doping of ~20 % Cu into the MOF structure results in an isostructural framework that is stable to activation and displays a high heat of adsorption for CO₂ (30.7 kJ mol⁻¹) as well as excellent CO₂/N₂ selectivity.

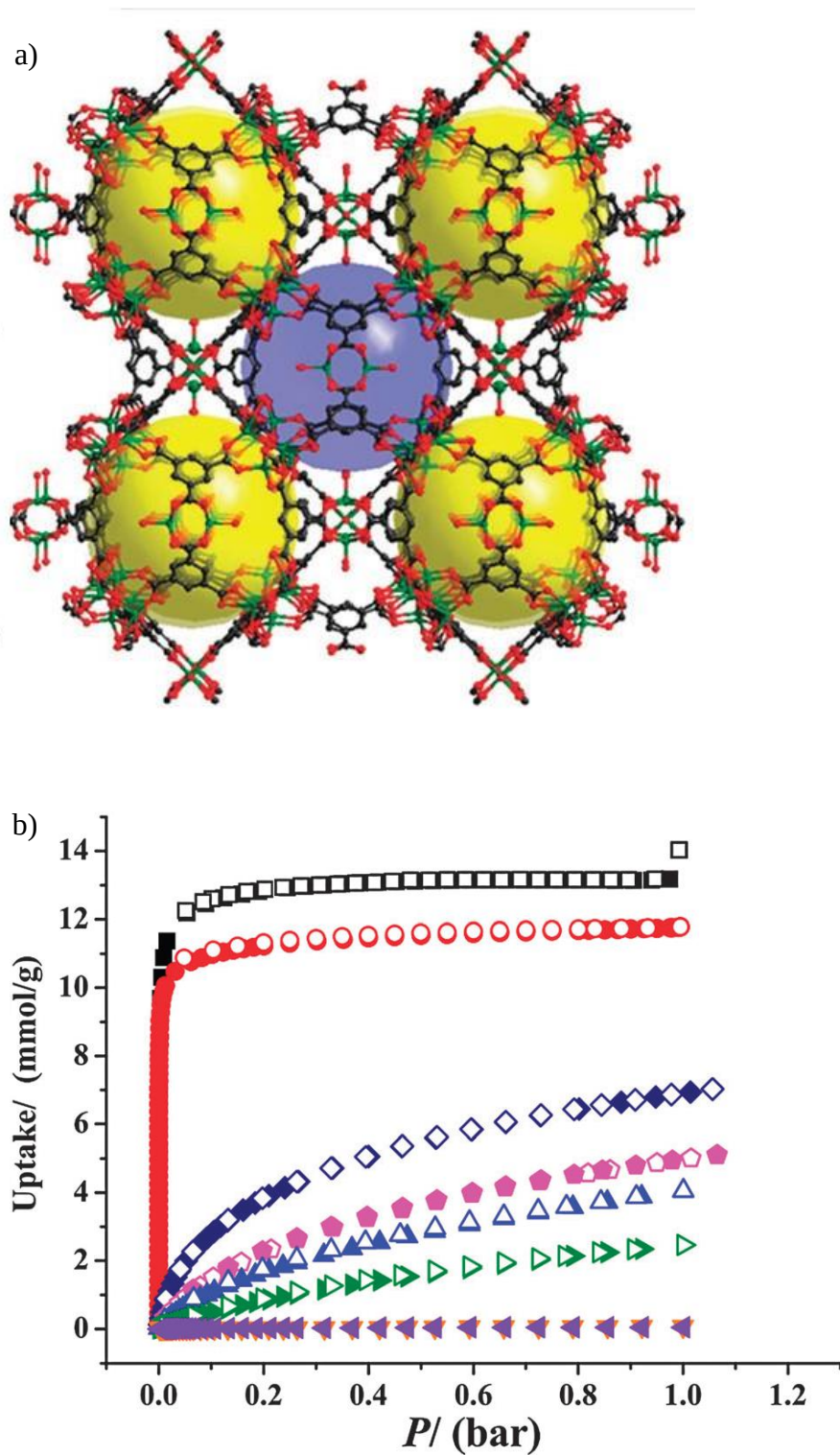


Fig. 3.5 a) View of the structure of $[\text{H}_2\text{N}(\text{CH}_3)_2]_2[\text{Zn}_{7.5}\text{Cu}_{1.5}(\mu_3\text{-OH})_2(\text{BTC})_6(\text{DMA})_3]$ b) Gas sorption isotherms (CO_2 – blue triangles, 273 K and green triangles, 298 K) (N_2 – orange triangles, 273 K and purple triangles, 298 K). Figures taken from reference 25.

One particular challenge when synthesising mixed metal MOFs solvothermally from different inorganic precursors is the requirement for the metals to react “together” to avoid the formation of solids based only on a single metal. The synthetic conditions used for NOTT-300Al and Cr are very similar, with the same temperature and similar reaction medium and times. Both MOFs display different gas sorption properties, particularly in terms of CO₂ selectivity. A mixed metal series of NOTT-300(AlCr) was synthesised and investigated to determine how changing the ratios of metal present affects the properties of these MOFs.

3.2 Results and Discussion

3.2.1 Synthesis of NOTT-300(AlCr) series

A series of heterometallic NOTT-300 MOFs has been synthesised containing varying ratios of Al:Cr. These are 2:1 ([Al_{1.3}Cr_{0.7}OH₂(C₁₆H₆O₈)]), 1:1 ([AlCrOH₂(C₁₆H₆O₈)] and 2:3 ([Al_{0.8}Cr_{1.2}OH₂(C₁₆H₆O₈)]). Different amounts of each starting material were combined and reacted under similar conditions to those used for the synthesis of both NOTT-300(Al) and NOTT-300(Cr), requiring high temperatures (210 °C) and long reaction times (3/4 days). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used as a screening process to confirm the desired amounts of metal were present owing to the questionable reproducibility of NOTT-300(Cr) and the difference in reactivity between the two metals. For both AlCr1:1 and AlCr2:3 frameworks, the ratio of starting material is equivalent to the ratio of the metals found in the product framework. The synthesis for AlCr2:1, however, required the presence of increased Al, a 4:1 ratio of Al:Cr was used to repeatedly obtain the desired

product. The reproducibility of these materials is varied, with some batches of reactions affording products with ratios in the desired range, others containing a wide range of metal content and some reactions only affording amorphous material. The products that did not contain the desired amounts of Al:Cr by ICP were discarded and not investigated further. There was limited progress made in optimising the synthesis, however, it was found that using AlCl_3 instead of $\text{Al}(\text{NO}_3)_3$ increased the likelihood of synthesising a crystalline product.

3.2.2 PXRD and IR Spectroscopy to Confirm Homogeneity

Powder X-ray diffraction (PXRD) was used to confirm the isostructural nature of the mixed metal materials and only small differences in the patterns were seen, due to slight changes in framework size (Table 3.1). All mixed metal MOFs display the NOTT-300 diffraction pattern and show single peaks with no splitting, indicating the presence of one homogeneous MOF consisting of two metals (Fig 3.6). Two single metal MOFs combined would display clear splitting of the peaks.

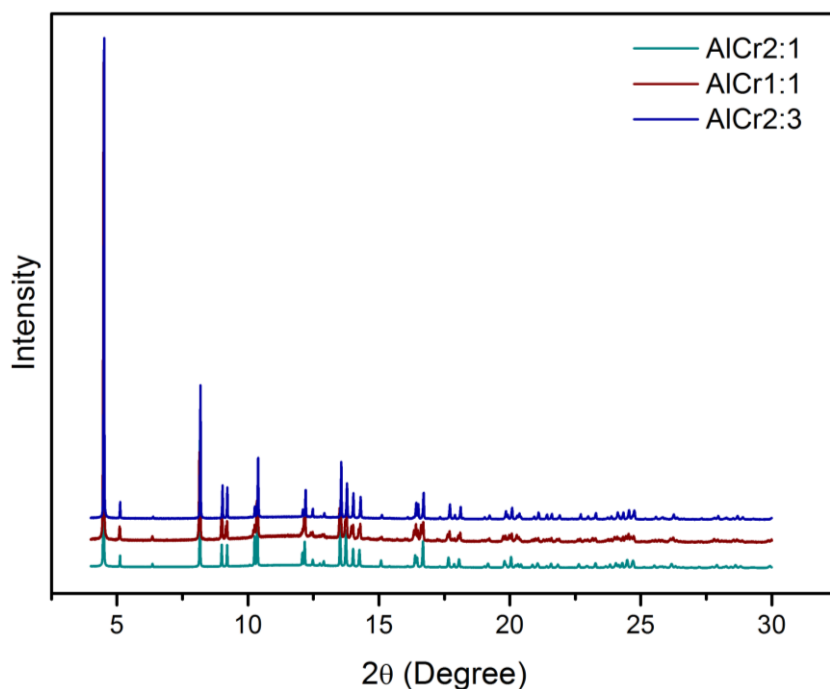


Fig. 3.6 PXRD patterns recorded for AlCr2:1, AlCr1:1 and AlCr2:3, $\lambda = 0.825633 \text{ \AA}$.

	$a=b \text{ (\AA)}$	$c \text{ (\AA)}$	Cell Volume ($\text{\AA}^3$)
AlCr2:1	14.83(3)	11.79(4)	2597.87(4)
AlCr1:1	14.88(4)	11.81(2)	2610.12(5)
AlCr2:3	14.92(2)	11.86(2)	2645.27(3)
NOTT-300(Cr)	14.99(2)	11.95(3)	2694.44(1)
NOTT-300(Al)	14.82(3)	11.76(3)	2589.50(1)

Table 3.1 – The unit cell parameters for AlCr2:1, AlCr1:1, AlCr2:3, NOTT-300(Cr) and NOTT-300(Al).

Although the structures of these MOFs are very similar, the potential differences in CO₂ adsorption properties are expected to arise from the cation content's effect on the bridging hydroxyl groups in the framework.

As ICP-OES only provides information on metal content in the sample and not on the connectivity of those metals, IR spectroscopy was used to probe all NOTT-300(AlCr) samples. IR spectroscopy allows us to see the different environments surrounding the bridging –OH groups. If the materials are just a combination of discrete NOTT-300(Al) and NOTT-300(Cr) crystallites two

peaks would be observed in the $\nu(\text{OH})$ region; one from $\text{Al}(\text{OH})\text{-Al}$ and one $\text{Cr}(\text{OH})\text{-Cr}$ (Fig.3.7).

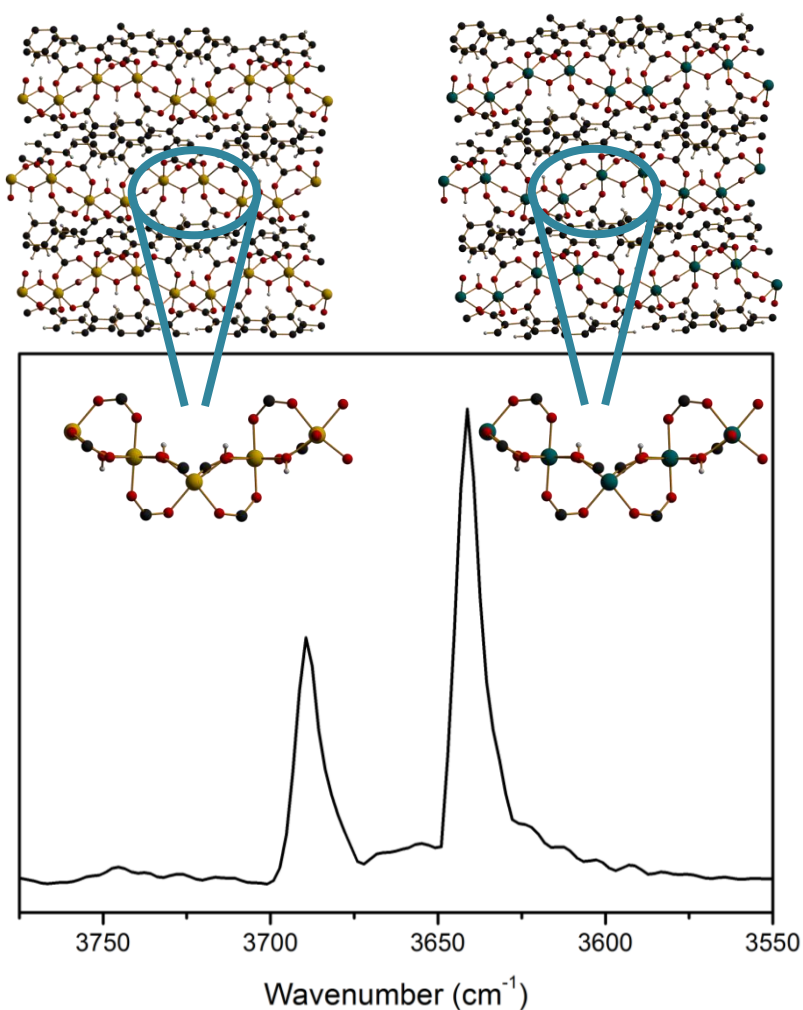
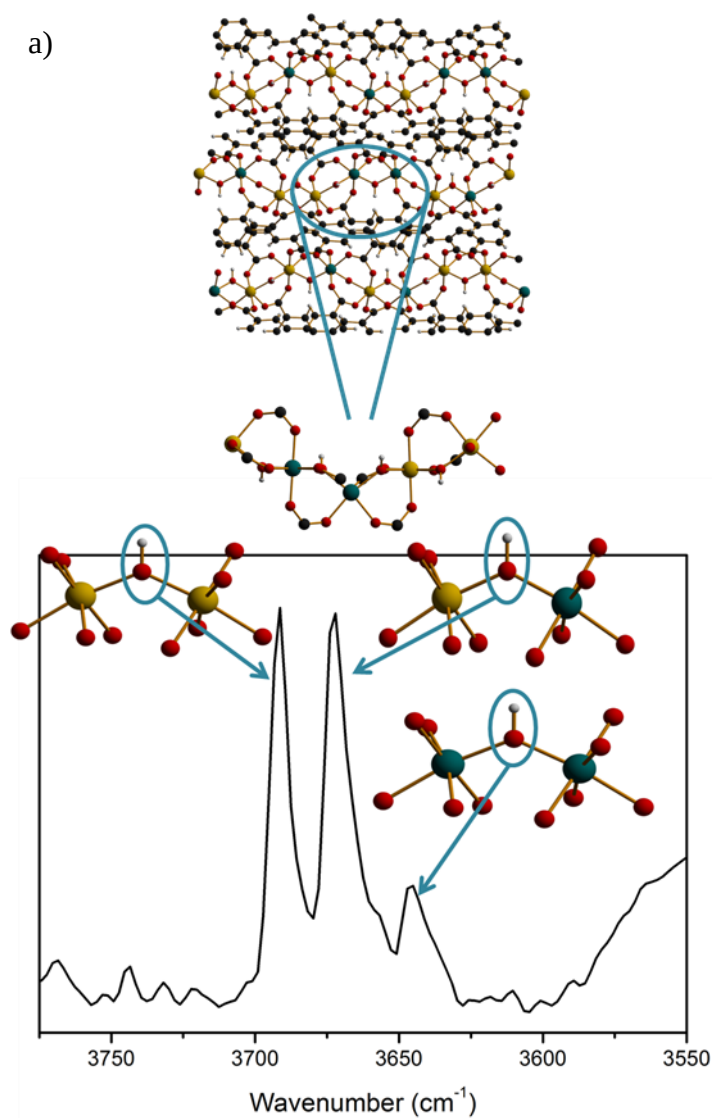


Fig. 3.7 Predicted IR spectrum for non-homogeneous mixed metal NOTT-300(AlCr) and a schematic of the -OH groups present. (Al – yellow, Cr – teal, C – grey, O – red, H – white).

$\text{AlCr}_{2:1}$ was analysed by synchrotron IR spectroscopy and three clear distinct peaks can be seen in the -OH region in the spectra at 3691, 3672 and 3645 cm^{-1} . Two of these peaks, 3691 and 3645 cm^{-1} , match well with those observed in the IR of NOTT-300(Al) and NOTT-300(Cr) respectively. These are assigned to the -OH groups bridging two of the same metal, Al-Al and Cr-Cr. The third peak can be assigned to the -OH that connects the two different metals. This proves

the material is a true mixed metal MOF and not merely a combination of the 2 single metal phases. The –OH peak for Cr-(OH)-Cr is the smallest peak, which is expected as with only ~33% Cr present in the structure the probability of Cr being located next to another Cr is lower than having either an adjacent Al-Al or Al-Cr.



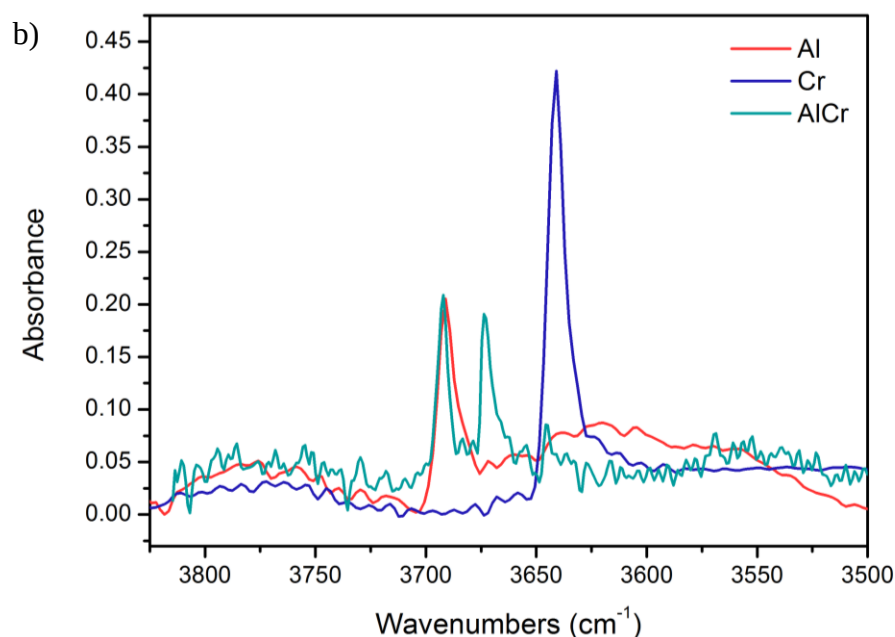


Fig. 3.8 a) IR spectrum of AlCr₂:1 and illustration of –OH groups present in the sample (Al - yellow, Cr – teal, C – grey, O – red, H – white), **b)** IR spectra of AlCr₂:1 and comparison to single metal NOTT-300(Al) and NOTT-300(Cr).

The ratio of the peak heights is approx. 1:1:0.3 (Al-OH-Al, 0.13; Al-OH-Cr, 0.13; Cr-OH-Cr, 0.04) which, assuming a truly homogeneous mixture of both metals in each crystallite, equates to an approximate metal content of 1.5:0.8 Al:Cr, and is in good agreement with result obtained by ICP (2:1).

This third –OH peak is also observed in the IR of AlCr₁:1 and AlCr₂:3, confirming these materials are also true mixed metal MOFs and not just combinations of NOTT-300(Al) and NOTT-300(Cr). The difference in metal content is reflected by the changing relative intensities of each M-(OH)-M peak, AlCr₁:1 displays more Al-(OH)-Cr than either Al-(OH)-Al or Cr-(OH)-Cr as would be expected. In the spectrum recorded for AlCr₂:3 it can be seen that the –OH peak attributed to the bridging of two Al centres is the least intense and therefore the least prevalent within the framework. The comparison of peak

height used to estimate the composition assumes that the extinction coefficient of the $\nu(\text{OH})$ remains the same in all three environments. The good agreement between the ratios calculated using this assumption and from both the synthesis and the ICP-OES results suggests this assumption is reasonable.

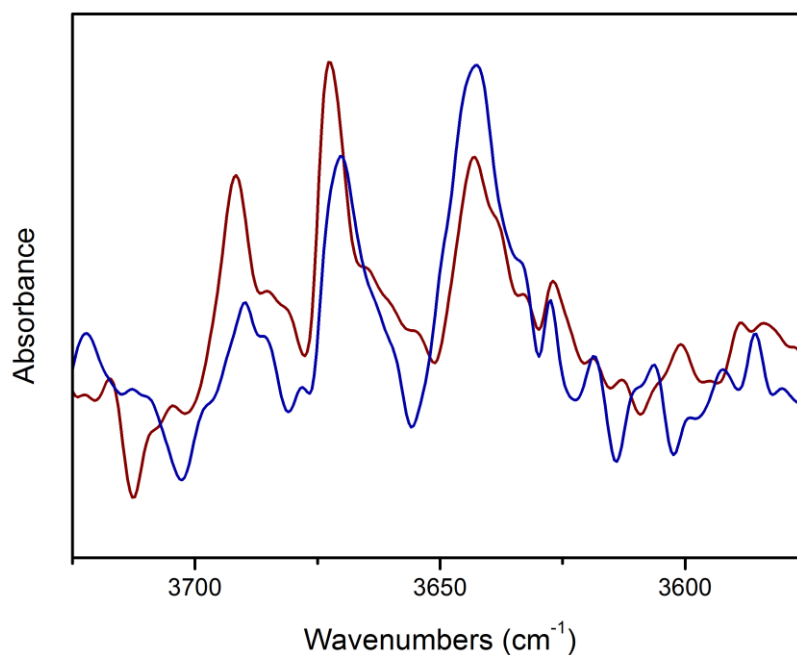


Fig. 3.9 IR spectra of AlCr1:1 (red) and AlCr2:3 (blue) showing presence of three $-\text{OH}$ peaks.

3.2.3 Thermal Stability

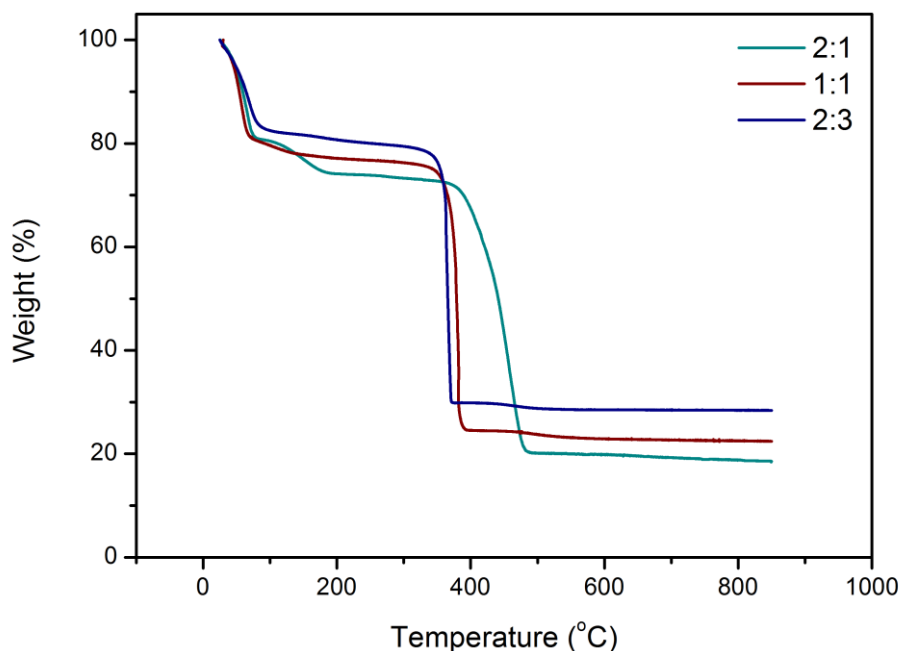


Fig. 3.10 TGA for AlCr2:1, AlCr1:1 and AlCr2:3 after acetone wash under N₂ atmosphere with a 5 °C a minute temperature ramp.

All samples show good thermal stability, as shown by TGA. All samples show solvent loss occurring before 200 °C, accounting for approximately 20 % mass, this is in good agreement with the single metal MOFs. All MOFs then remain stable until 330 °C with AlCr2:3 then decomposing. It was found that AlCr2:1 had the highest thermal stability, decomposing at 375 °C. When investigating the single metal MOFs, it was found that NOTT-300(Cr) had the highest thermal stability when studied by TGA, which would lead to the assumption that a higher Cr content would lead to a higher thermal stability. However, this is not what is observed with these mixed metal materials. The mixed MOF with the highest Al content has the highest thermal stability. It is reasonable to assume that the mixed metal MOFs do not just display a summative combination of characteristics

depending on the metal content, but instead have their own properties especially since they contain the new Al-(OH)-Cr motif.

3.2.4 Gas Adsorption Properties of Series

3.2.4.1 H₂ and N₂ Adsorption

To investigate whether “fine control” over the gas adsorption properties of NOTT-300 through changing the metal content is possible a series of adsorption isotherms (H₂, CO₂, CH₄ *etc.*) were measured for all ratios. N₂ isotherms were measured at 77 K and a clear trend appears, with the adsorption increasing with increasing amounts of Cr in the framework. AlCr₂:3 reaches an uptake of 2.68 mmol g⁻¹ (60.03 cc g⁻¹), which, although the highest adsorbed amount by the mixed metal series, is relatively low for porous MOFs.

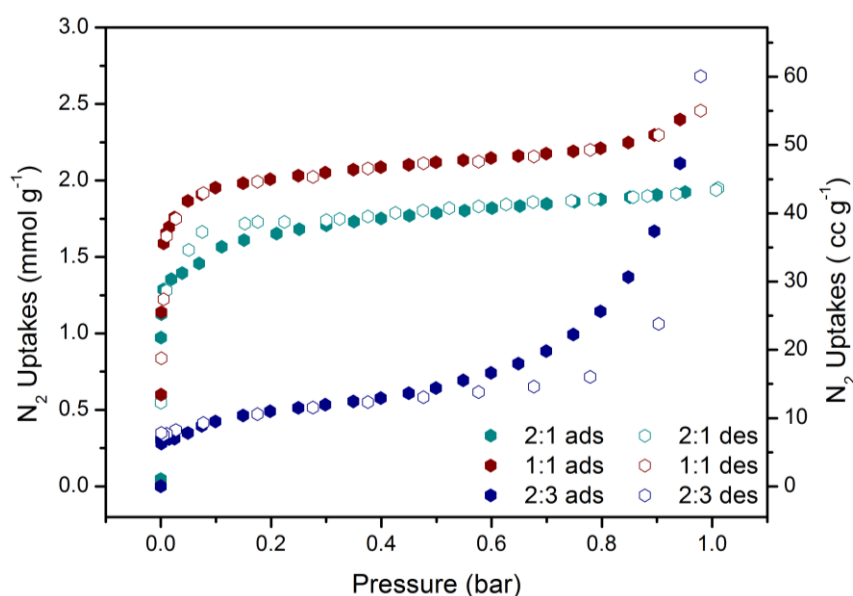


Fig. 3.11 N₂ adsorption isotherms for all NOTT-300AlCr materials recorded at 77 K and 0 – 1 bar.

The shapes of the N₂ adsorption isotherms are different for the three MOFs. AlCr₂:1 displays a type-I shape, with steep uptakes at low pressures then

gradually reaching a plateau as saturation is achieved. AlCr₂:3 shows a sharp increase in uptakes at higher pressures, and is almost a type-II shape. AlCr₁:1 appears to contain characteristics of the shapes displayed by both AlCr₂:1 and 2:3, with a large uptake at low pressures, reaching a plateau (type – I) and then again displaying an increase above 0.8 bar (type – II) although not as large as the one observed for 2:3.

H₂ adsorption measurements were carried out at 77 K (all AlCr_s) and 87 K (AlCr₂:1 and AlCr₂:3) up to 20 bar. There appears to be a significant difference between the H₂ uptakes displayed by 2:1 compared to those for 1:1 and 2:3 (Fig. 3.12). With AlCr₂:1 reaching an uptake of 11.58 mmol g⁻¹ at 77 K and 20 bar, whereas both AlCr₁:1 and AlCr₂:3 exhibit much lower uptake under the same conditions, only reaching 3.02 and 3.48 mmol g⁻¹ respectively. These results go against the expected trend of increased uptake with increased Cr content because of the increased size/space. On increase of temperature to 87 K the AlCr₂:1 displays lower uptake of H₂ (8.48 mmol g⁻¹), as expected, however the uptake for AlCr₂:3 almost doubles (6.05 mmol g⁻¹). This makes the difference in uptake at 1 bar between AlCr₂:1 and AlCr₂:3 smaller, with only a difference of ~2.5 mmol g⁻¹ compared to a difference of 8 mmol g⁻¹ observed at 77 K. This large increase in adsorption with increase in temperature is unusual and could benefit from being remeasured in order to establish what is occurring is “real”.

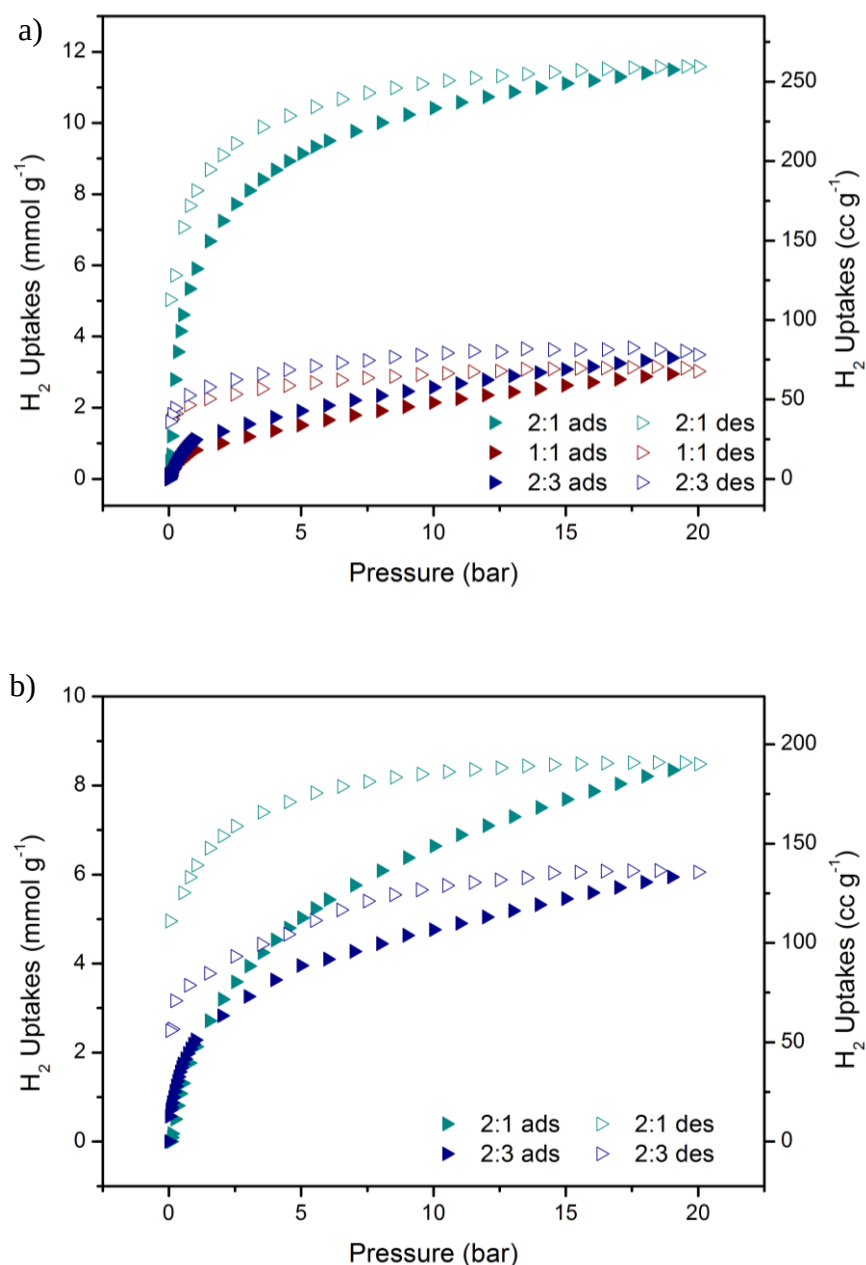


Fig. 3.12 H₂ adsorption isotherms measured for AlCr2:1, AlCr1:1 and AlCr2:3 from 0 – 20 bar at **a)** 77 K, **b)** 87 K.

3.2.4.2 CO₂ Adsorption

At 195 K and 1 bar the CO₂ adsorption behaviour of the three mixed metal MOFs display significant differences in uptake. AlCr2:1 has the highest CO₂ uptake under these conditions and AlCr2:3 displays the lowest adsorption capacity for CO₂ with uptakes of 10.60 and 6.11 mmol g⁻¹, respectively. All isotherms display

type-I behaviour and some degree of hysteresis upon desorption. AlCr2:1 not only displays the highest uptake, but also the smallest hysteresis upon desorption. The lower uptakes and larger hysteresis observed with both AlCr1:1 and AlCr2:3 are likely to be caused by the same reason; however it is not fully understood at this time.

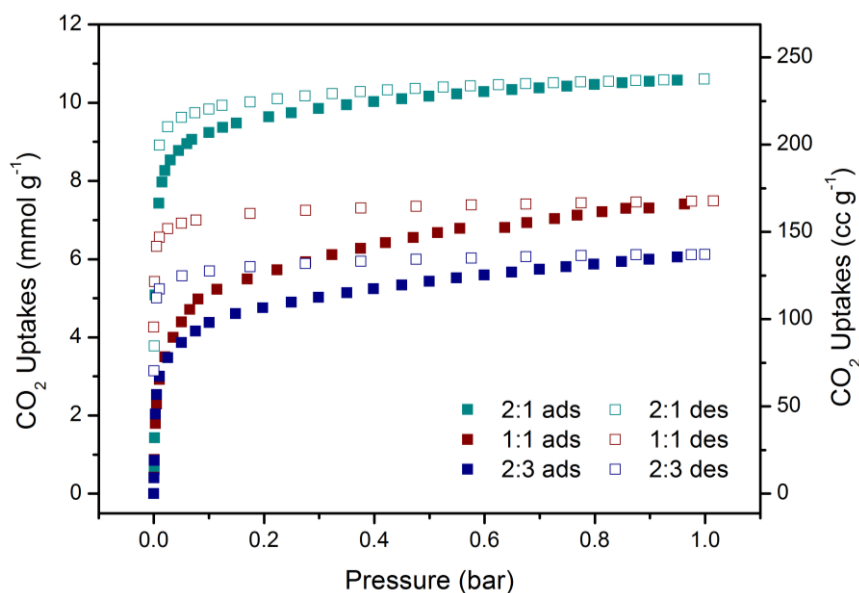


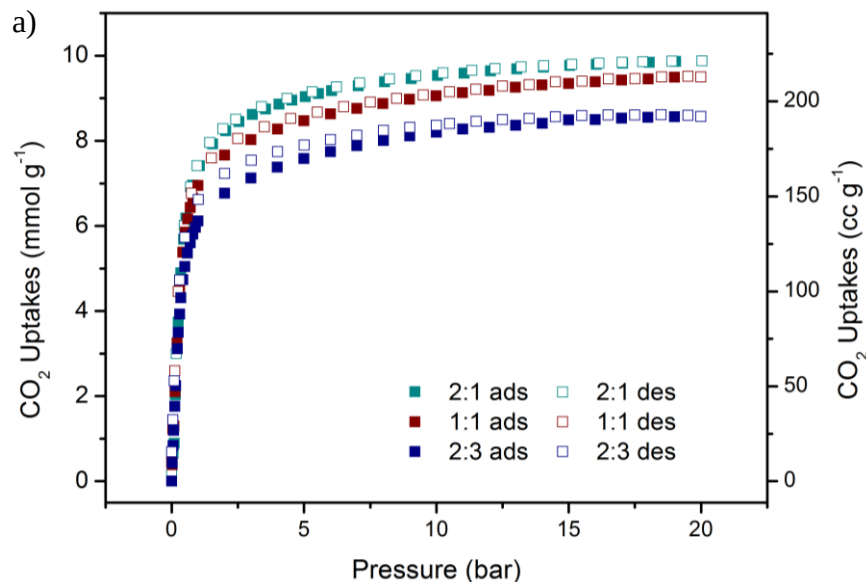
Fig. 3.13 CO₂ adsorption isotherms recorded at 195 K and 0 – 1 bar for AlCr2:1, AlCr1:1 and AlCr2:3.

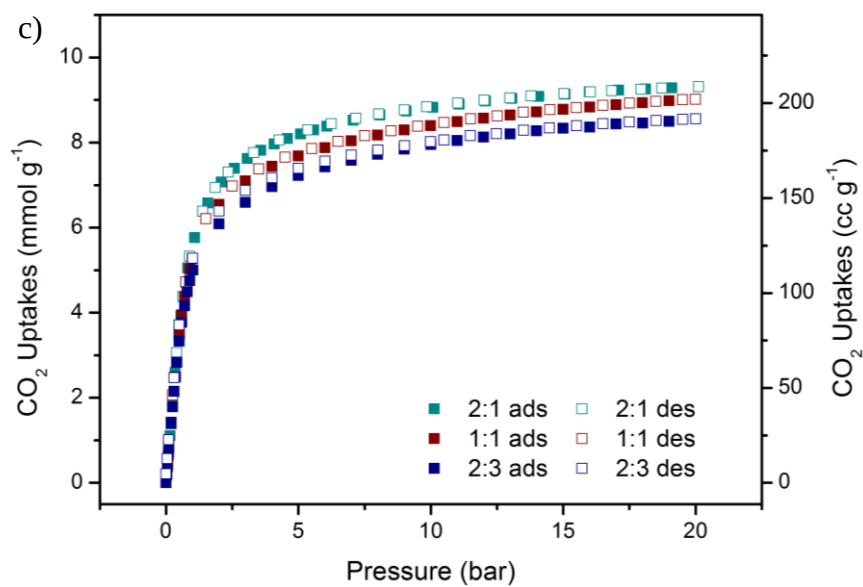
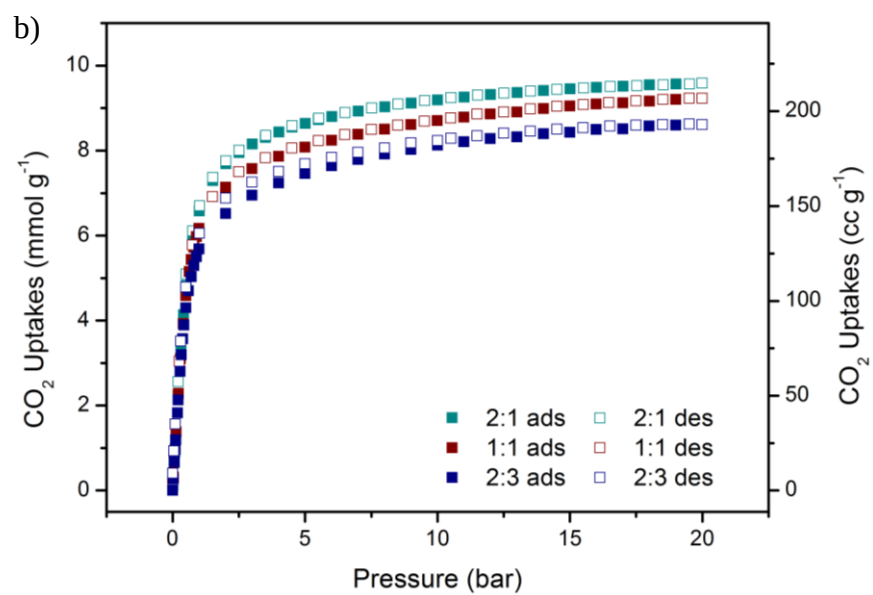
The CO₂ adsorption isotherms carried out at higher temperatures (273-303 K) display smaller differences between the three mixed metal samples. Both AlCr2:1 and AlCr1:1 reach uptakes over 9 mmol g⁻¹ at 273 K and 20 bar (9.87 and 9.50 mmol g⁻¹ respectively). Although lower, AlCr2:3 still displays high adsorption capacity for CO₂ under these conditions, with an uptake of 8.57 mmol g⁻¹. For AlCr2:1 there is a decrease in adsorption from 195 → 273 K whereas for both AlCr1:1 and AlCr2:3 the adsorption increases from 195 → 273 K. Both mixed metal MOFs with equal or higher amounts of Cr (AlCr1:1 and AlCr2:3) appear to be displaying the behaviour previously observed in NOTT-300(Al) and

not NOTT-300(Cr) which was more expected. This clearly demonstrates that each material has unique properties that are not merely a summative combination of the single metal materials. The presence of the new bridging -OH group (Al-OH-Cr) affects the CO₂ adsorption due to the new interactions present. There does not appear to be a trend based on either metal content nor does there appear to be a trend based on the amount of each -OH group present.

CO ₂ Uptake (mmol g ⁻¹)	AlCr2:1	AlCr1:1	AlCr2:3
195 K	10.60	7.49	6.11
273 K	9.87	9.50	8.57
283 K	9.58	9.23	8.61
293 K	9.31	9.02	8.56
303 K	8.99	8.78	8.41

Table 3.2 – The recorded CO₂ uptake for AlCr2:1, AlCr1:1 and AlCr2:3 at 20 bar, 195 K data recorded at 1 bar.





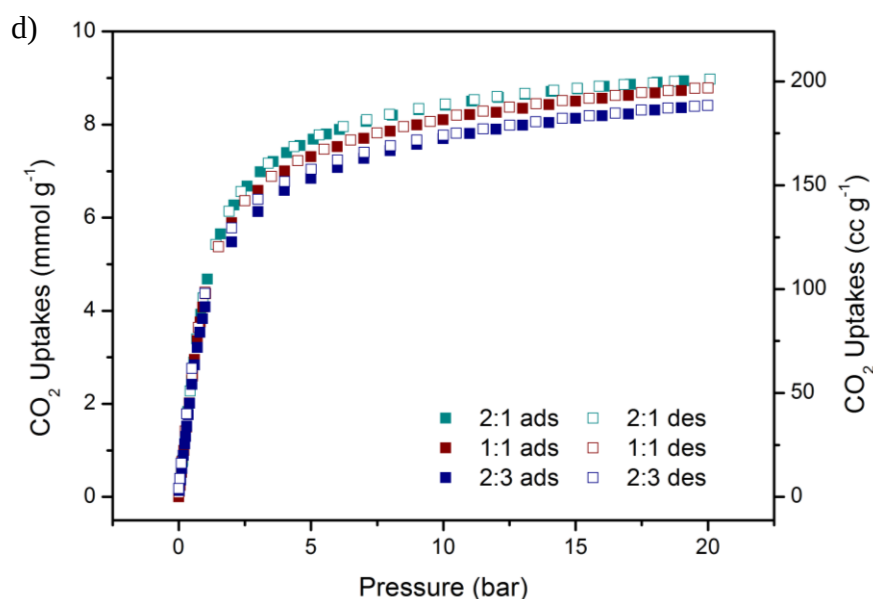


Fig. 3.14 CO₂ adsorption isotherms carried out from 0 – 20 bar for AlCr2:1, AlCr1:1 and AlCr2:3 at **a)** 273 K, **b)** 283 K, **c)** 293 K, **d)** 303 K.

AlCr2:1 exhibits the highest affinity for CO₂ out of the mixed metal MOFs at all temperatures recorded up to 20 bar. The CO₂ adsorption in AlCr2:1 was further studied by carrying out CO₂ adsorption isotherms at increased temperatures, up to 370 K. Material stability and retention of adsorption capacity for CO₂ at higher temperatures could be key for future potential use in separation applications that may require increased temperatures. AlCr2:1 appears to maintain its high adsorption capacity for CO₂ at elevated temperatures with uptake of 7.01 and 6.43 mmol g⁻¹ at 353 K and 370 K respectively.

CO ₂ uptake (mmol g ⁻¹)	273 K	283 K	293 K	298 K	303 K	313 K	333 K	353 K	370 K
AlCr2:1	9.87	9.58	9.31	9.14	8.99	8.60	7.85	7.01	6.43

Table 3.3 – The CO₂ uptake for AlCr2:1 at 20 bar for all temperatures recorded.

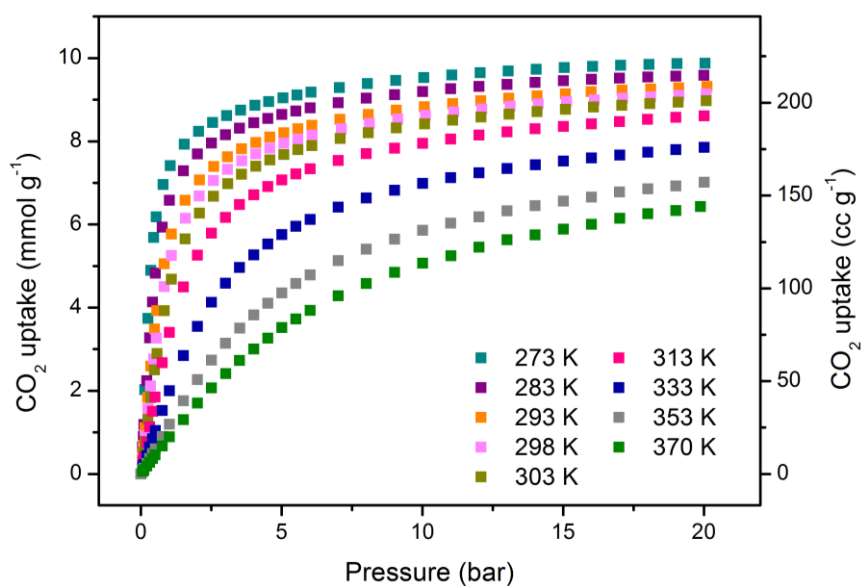


Fig. 3.15 All recorded CO₂ adsorption isotherms for AlCr₂:1 displaying high CO₂ adsorption capacity even at elevated temperatures.

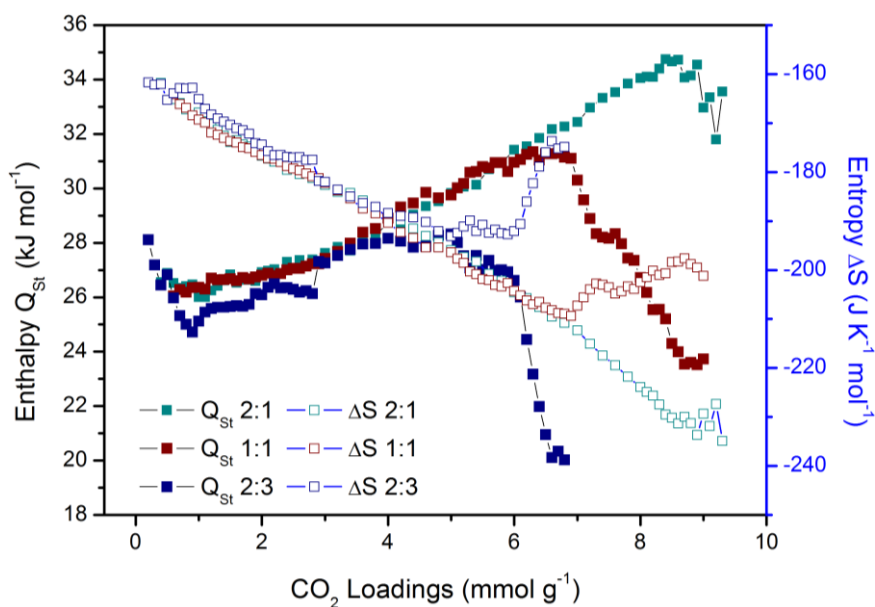


Fig. 3.16 Isothermic heat of adsorption and entropy for CO₂ loading in NOTT-300(AlCr) series.

The calculated heats of adsorption give some insight into the differences of CO₂ uptakes by the mixed metal MOFs. At low loadings the three MOFs appear to have similar heats of adsorption (~ 26 – 27 kJ mol⁻¹) and follow the same trend of increased enthalpy with increased loadings. The heat of adsorption for AlCr₂:1 continues to increase with increased loading, reaching 34.5 kJ mol⁻¹, leading to

the conclusion that even at higher loadings further adsorption is favourable. This is when CO₂-CO₂ interactions play a more dominant role in the uptakes than CO₂-framework interactions. The decrease in enthalpy shown for AlCr1:1 and AlCr2:3 at increased loadings could possibly indicate there are no such CO₂-CO₂ interactions able to be formed in these materials.

	AlCr2:1	AlCr1:1	AlCr2:3
Enthalpy (kJ mol ⁻¹)	26.5 - 34.5	26.0 - 23.7 (31)	27.2 - 20.0 (28)
Entropy (J K ⁻¹ mol ⁻¹)	-161 – -233	-164 – -201	-162 – -152

Table 3.4 – The heats of adsorption for CO₂ adsorption in AlCr2:1, AlCr1:1 and AlCr2:3. () denote highest enthalpy reached.

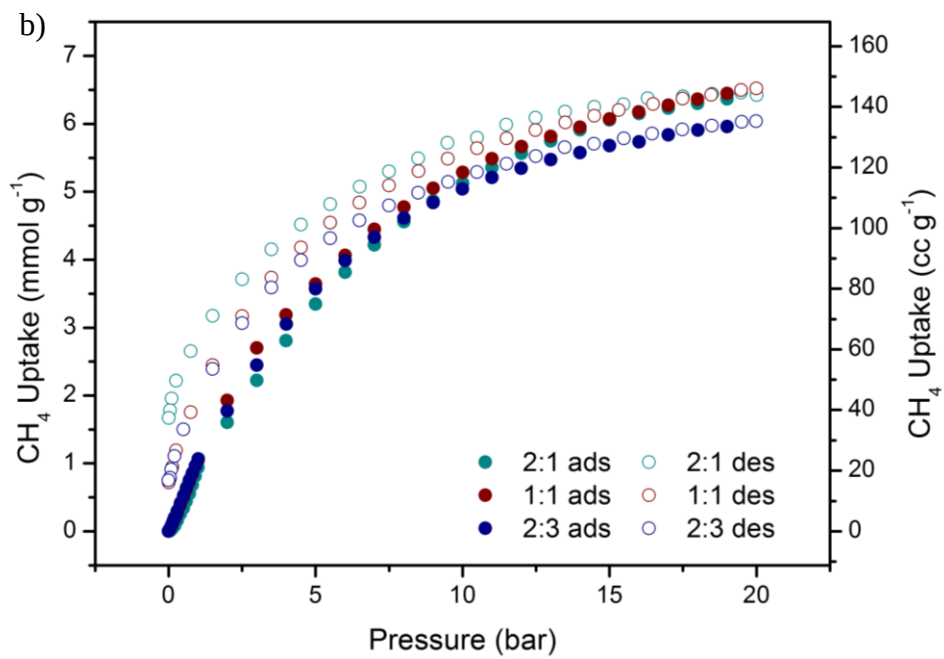
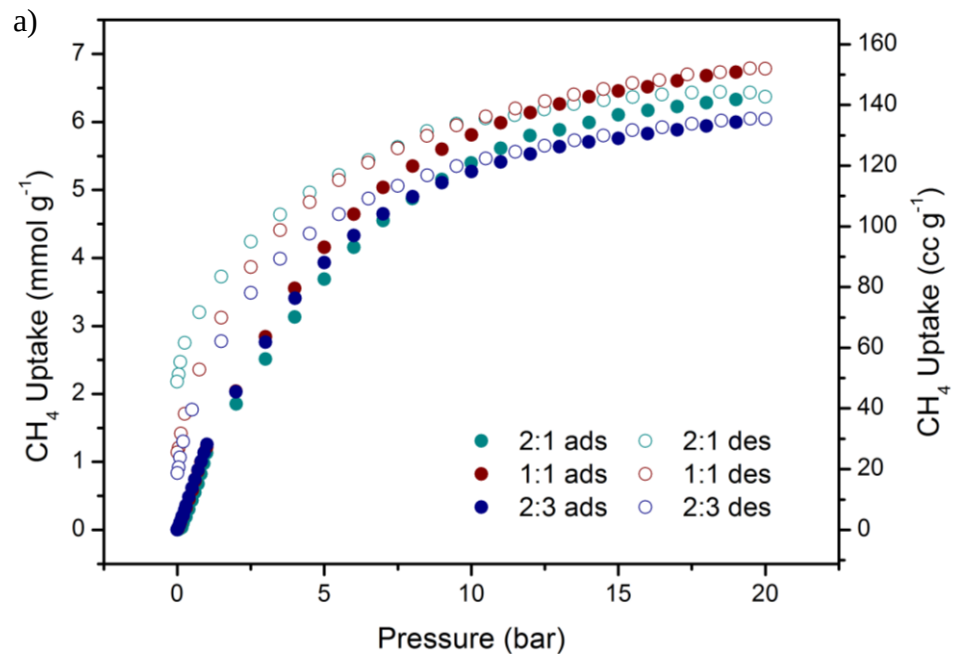
3.2.4.3 NOTT-300(AlCr)s Vs. NOTT-300(Al) and NOTT-300(Cr)

When compared to the behaviours of NOTT-300(Al) and NOTT-300(Cr), the CO₂ adsorption for the mixed metal series is interesting. NOTT-300(Cr) possesses a higher adsorption capacity for CO₂ than NOTT-300(Al) attributed to, in part, the increased size and therefore increased available space for adsorption. Therefore a trend of increased adsorption with increased Cr content is reasonable to predict, however, this is not what is observed. At nearly all temperatures AlCr2:1 displays the highest CO₂ adsorption capacity of the mixed metal MOFs. AlCr2:3, the MOF with the highest Cr content, displays the lowest. Perhaps this is showing that properties arising from mixed metal MOFs are not merely an averaged combination of the two single metal MOFs, as a new –OH moiety is present that will have its own interactions and contributions towards overall uptake capacity and interactions. Another difference in adsorption behaviour is the difference in uptake at low temperature (195 K) compared with more ambient temperatures (273 K). NOTT-300Al exhibits almost no uptake of

any gas at low temperatures and the CO₂ uptake at 195 K and 1 bar (2.95 mmol g⁻¹) is significantly lower than the uptake observed at 273 K (7 mmol g⁻¹). The opposite is observed for NOTT-300Cr since the highest CO₂ uptake recorded for this framework, 10.95 mmol g⁻¹, was achieved at 195 K and 1 bar. It was therefore expected that AlCr₂:1 would exhibit similar behaviour to NOTT-300(Al) and for AlCr₂:3 to behave in a similar fashion to NOTT-300(Cr). However, the opposite is observed, with AlCr₂:1 having higher adsorption capacity for CO₂ at 195 K and AlCr₂:3 displaying higher uptakes at more ambient temperatures. The latter is also observed for AlCr₁:1.

3.2.4.4 CH₄ Adsorption

A series of CH₄ isotherms were measured and all three MOFs display similar uptake, however, there is no discernible trend with respect to the ratio of metals as the adsorption varies with respect to temperature. At 273 K and 20 bar AlCr₁:1 displays the highest uptake, reaching 6.78 mmol g⁻¹, and AlCr₂:3 the lowest, 6.04 mmol g⁻¹. However, when the temperature is increased to 303 K it is AlCr₂:3 that exhibits the highest CH₄ uptake of 6.20 mmol g⁻¹.



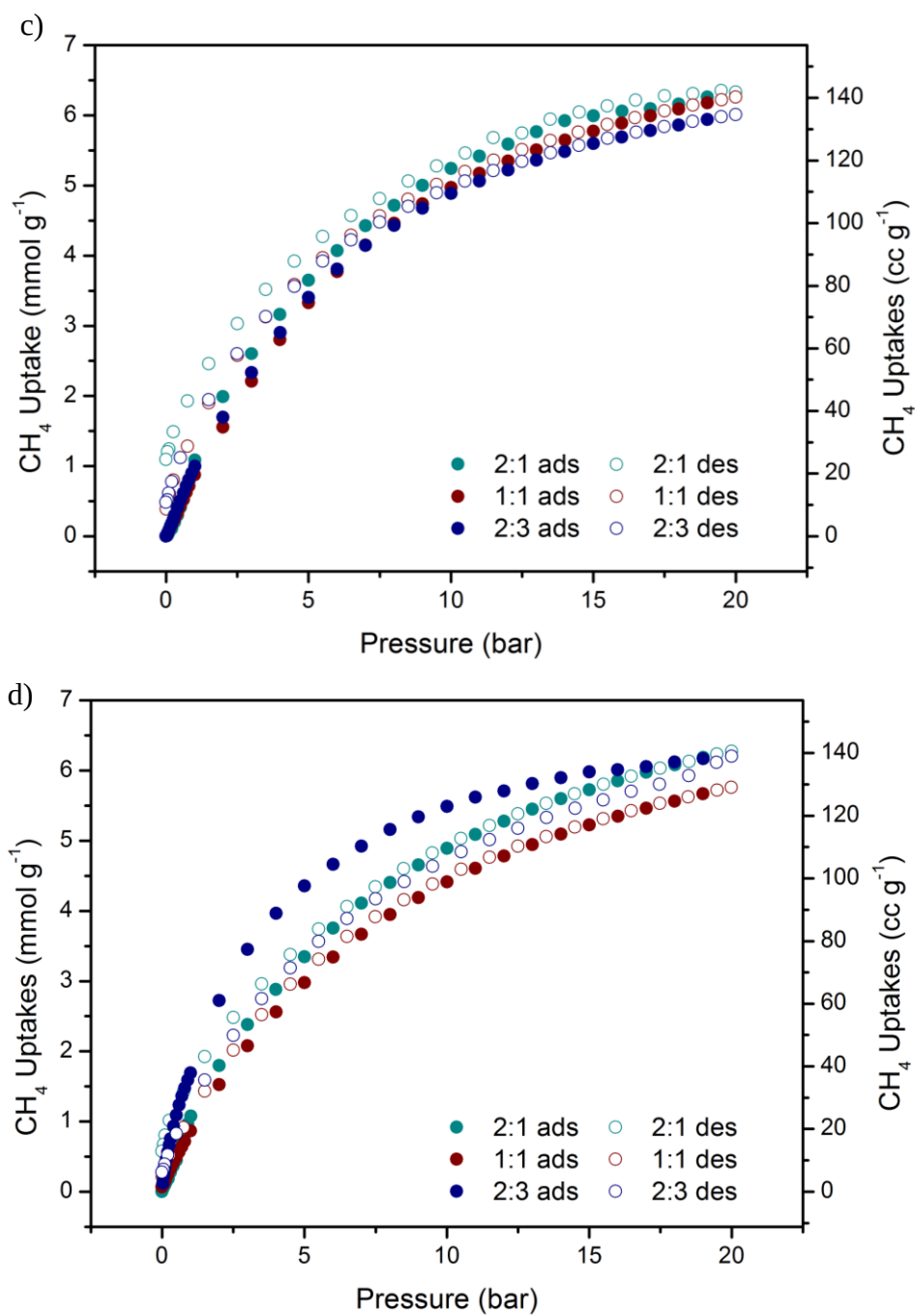


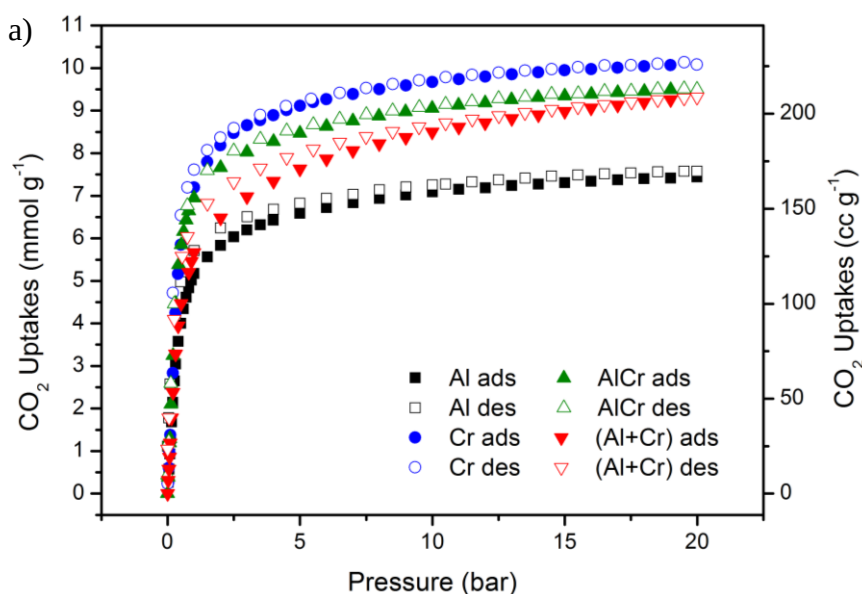
Fig. 3.17 CH₄ adsorption isotherms carried out from 0 – 20 bar for AlCr₂:1, AlCr₁:1 and AlCr₂:3 at **a)** 273 K, **b)** 283 K, **c)** 293 K, **d)** 303 K.

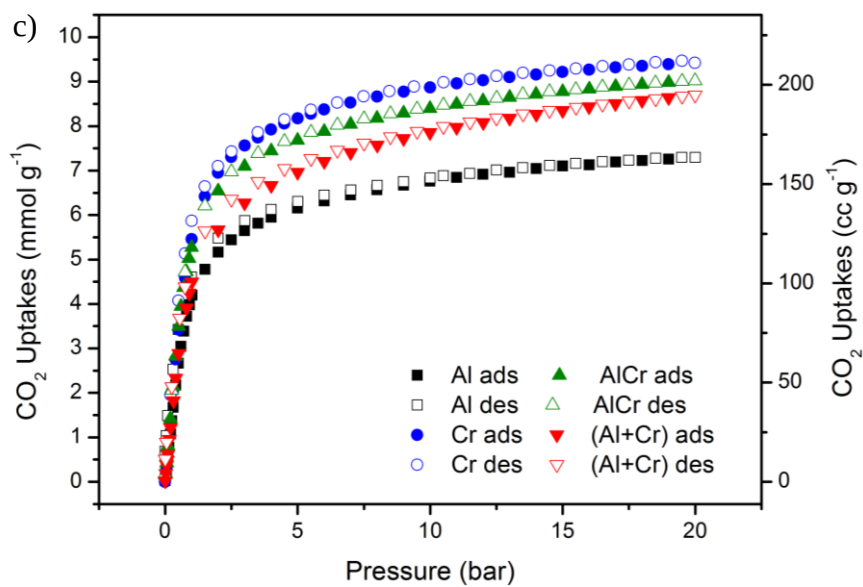
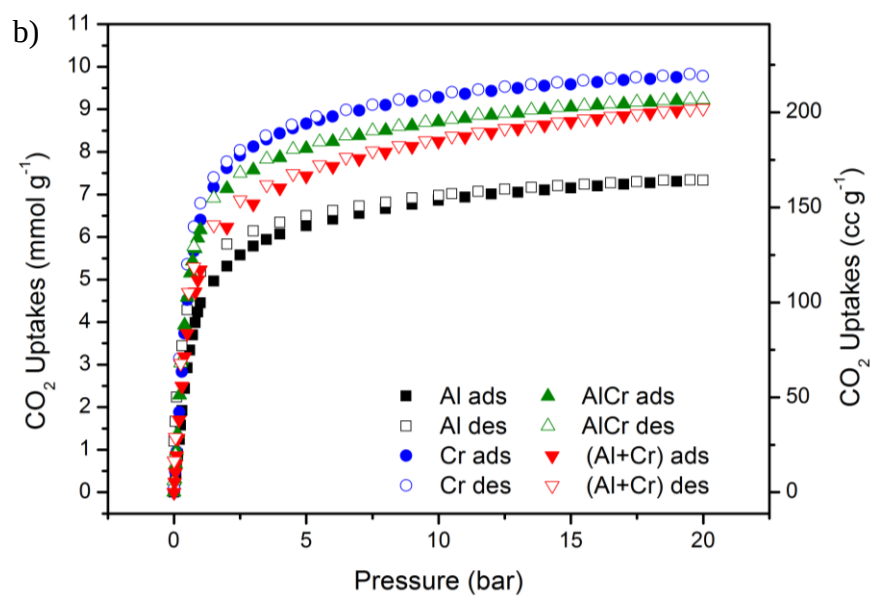
CH ₄ uptake (mmol g ⁻¹)	AlCr2:1	AlCr1:1	AlCr2:3
273 K	6.37	6.78	6.04
283 K	6.42	6.52	6.04
293 K	6.33	6.26	6.01
303 K	6.27	5.76	6.20

Table 3.5 – The recorded CH₄ uptake for AlCr2:1, AlCr1:1 and AlCr2:3 at 20 bar.

3.3.4.5 Gas (CO₂, CH₄) Adsorption in a Mechanical Mix of NOTT-300(Al) and NOTT-300(Cr)

To examine whether the properties of the mixed metal NOTT-300AlCr_s are truly from a novel system, or merely just a combination of the single metal material's properties, samples of NOTT-300(Al) and NOTT-300(Cr) were combined in a 1:1 molar ratio (NOTT-300Al+Cr) and the gas adsorption properties (CO₂ and CH₄) were examined. Samples of NOTT-300(Al) and NOTT-300(Cr) were weighed and thoroughly mixed until a single consistent colour was observed throughout the entire sample. ICP was used to confirm the content of the metals present in the sample (1:1).





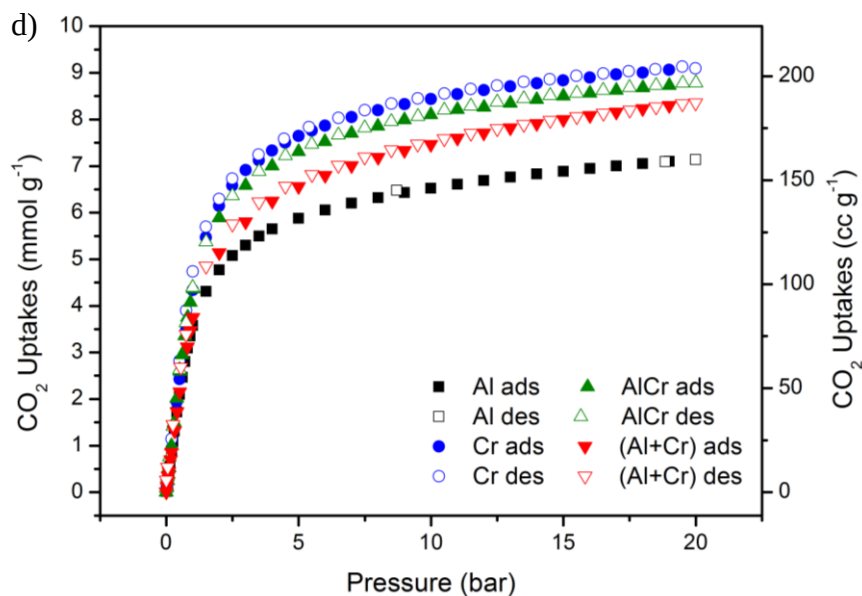


Fig. 3.18 CO₂ adsorption isotherms carried out from 0 – 20 bar for NOTT-300(Al), NOTT-300(Cr), AlCr1:1 and [Al+Cr] at **a)** 273 K, **b)** 283 K, **c)** 293 K, **d)** 303 K.

The recorded CO₂ uptakes (273 – 303 K) for this mechanical mix of NOTT-300, named [Al+Cr], are similar to the mixed metal MOF. However, at all temperatures recorded AlCr1:1 displays higher uptakes than [Al+Cr], indicating the higher presence of Al-OH-Al in [Al+Cr] does in fact limit the adsorption process. These differences in adsorption become larger at higher temperatures.

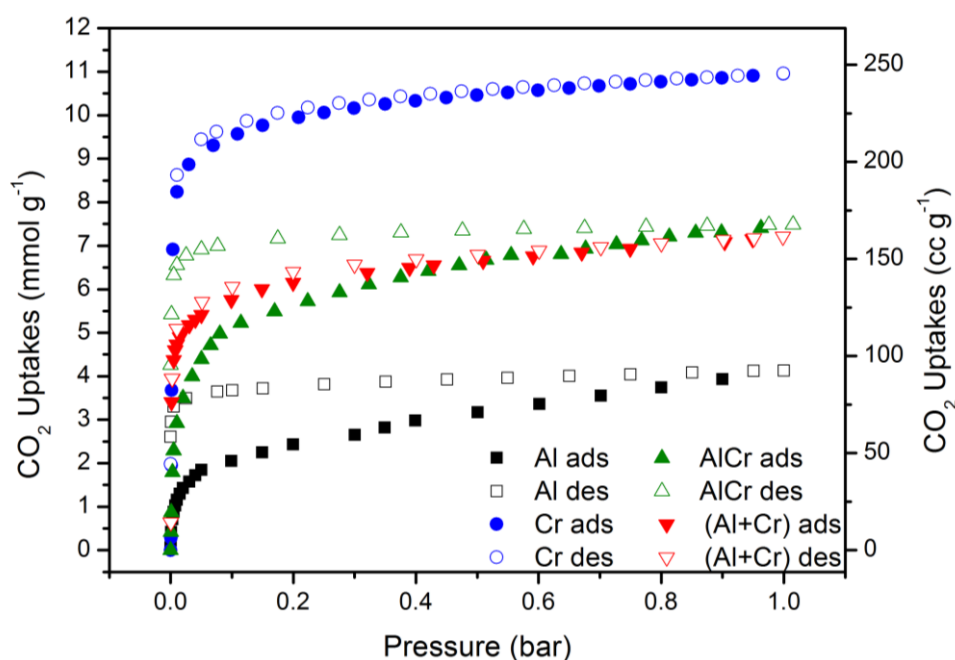


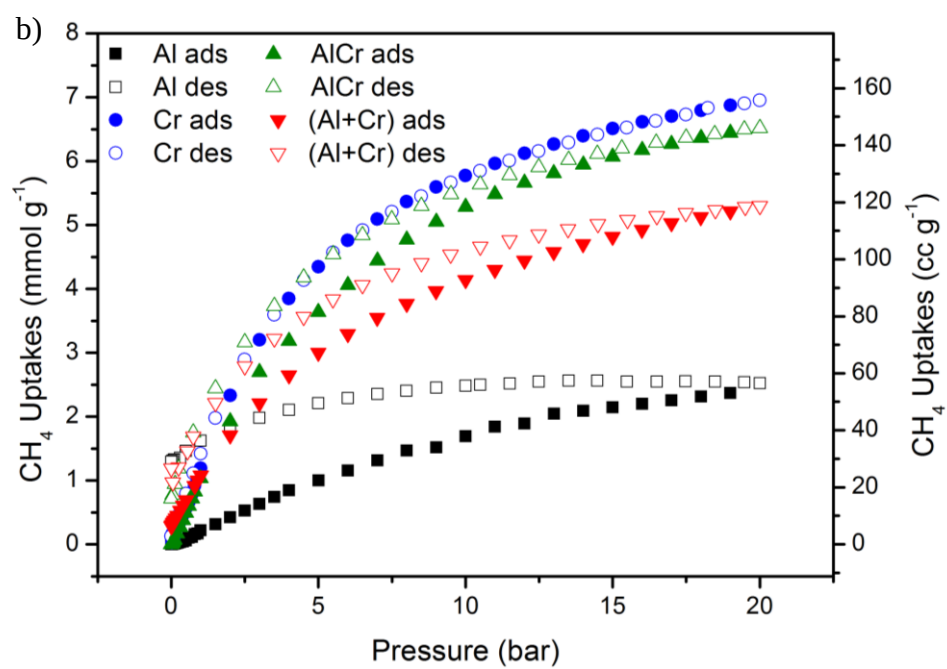
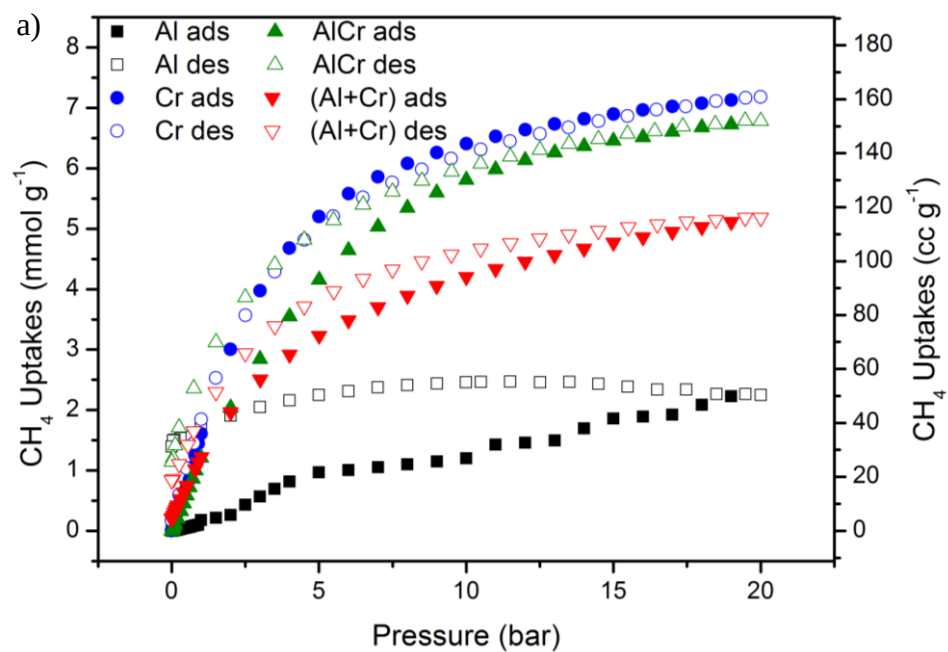
Fig. 3.19 CO₂ adsorption isotherm carried out from 0 – 1 bar at 195 K for NOTT-300(Al), NOTT-300(Cr), AlCr1:1 and [Al+Cr].

The CO₂ adsorption isotherm measured at 195 K and 0 – 1 bar shows some interesting features. The overall uptake achieved for both AlCr and [Al+Cr] is very similar (7.49 and 7.21 mmol g⁻¹ respectively) and both display a degree of hysteresis upon desorption. It can be seen that under these conditions NOTT-300Al has a large hysteresis upon desorption and for Cr the desorption closely follows the adsorption, with no observable hysteresis. It would be expected for [Al+Cr] to display hysteresis, somewhere in between the two single metal MOFs, however the hysteresis for this material is much smaller than that displayed for AlCr.

CO ₂ Uptake (mmol g ⁻¹)	NOTT-300(Al)	AlCr1:1	[Al+Cr]	NOTT-300(Cr)
195 K	4.13	7.49	7.21	10.95
273 K	7.57	9.50	9.31	10.08
283 K	7.33	9.23	9.02	9.78
293 K	7.29	9.02	8.69	9.42
303 K	7.14	8.78	8.35	9.09

Table 3.6 – The recorded CO₂ uptake for NOTT-300(Al), NOTT-300(Cr), AlCr1:1 and [Al+Cr] at 20 bar.

The differences in CO₂ adsorption observed for AlCr and [Al+Cr] are very slight, this is most likely caused by the similar CO₂ uptakes displayed by the single metal MOFs. A series of CH₄ adsorption isotherms were also measured, as the CH₄ adsorption for NOTT-300(Al) and NOTT-300(Cr) is very different, with NOTT-300(Al) having a very low uptake for CH₄, 2 mmol g⁻¹ or less. NOTT-300(Cr) has a much higher adsorption of CH₄ and hence it is easier to see if properties arise from a summative combination of the two single metal MOFs or if the properties arise from the MOF itself, as a solid solution. At all temperatures recorded, there is a clear difference in adsorption behaviour between AlCr and [Al+Cr]. AlCr displays relatively high CH₄ adsorption, similar to that reached by NOTT-300(Cr). [Al+Cr] adsorption appears to lie in the middle of the adsorption for NOTT-300(Cr) and NOTT-300(Al) showing it clearly does possess a combination of the properties of NOTT-300(Al) and NOTT-300(Cr) whereas AlCr1:1 displays unique properties. NOTT-300(Al) displays hysteresis upon desorption at all temperatures and there is a degree of hysteresis also displayed by AlCr1:1 at 273 K, however at higher temperatures (303 K) the adsorption is fully reversible. [Al+Cr] also displays hysteresis and like NOTT-300(Al), this occurs at all temperatures.



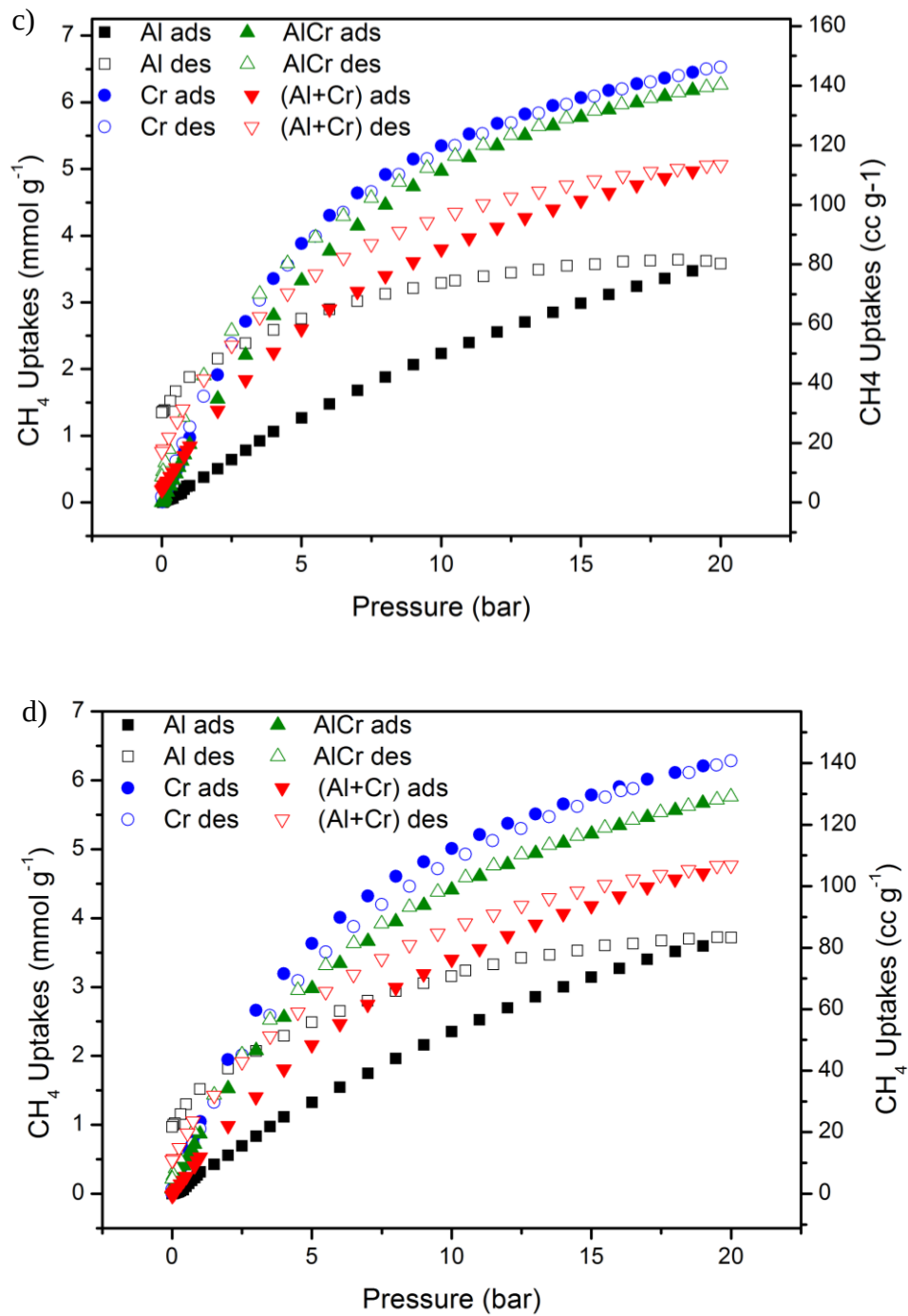


Fig. 3.20 CH₄ adsorption isotherms carried out from 0 – 20 bar for NOTT-300(Al), NOTT-300(Cr), AlCr1:1 and [Al+Cr] at **a)** 273 K, **b)** 283 K, **c)** 293 K, **d)** 303 K.

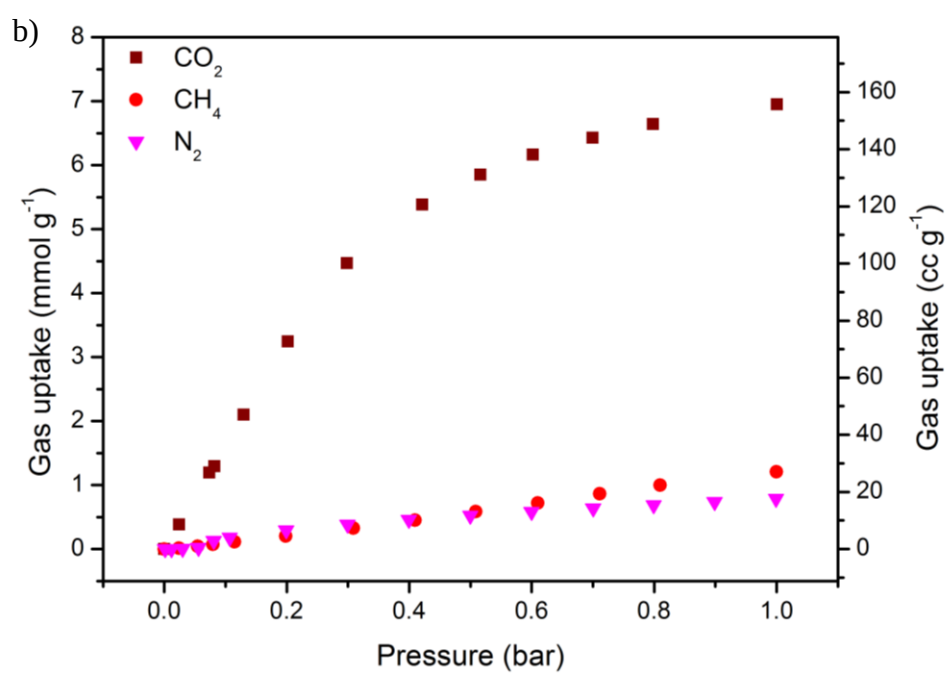
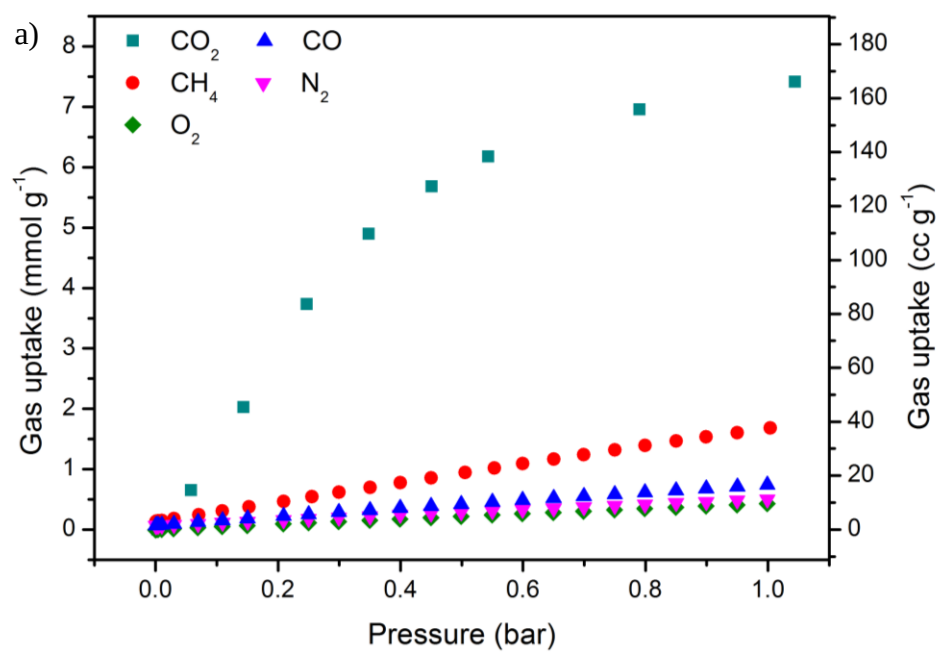
CH ₄ Uptake (mmol g ⁻¹)	NOTT-300(Al)	AlCr1:1	[Al+Cr]	NOTT-300(Cr)
273 K	2.24	6.78	5.18	7.18
283 K	2.52	6.52	5.30	6.95
293 K	3.58	6.26	5.06	6.52
303 K	3.72	5.76	4.76	6.28

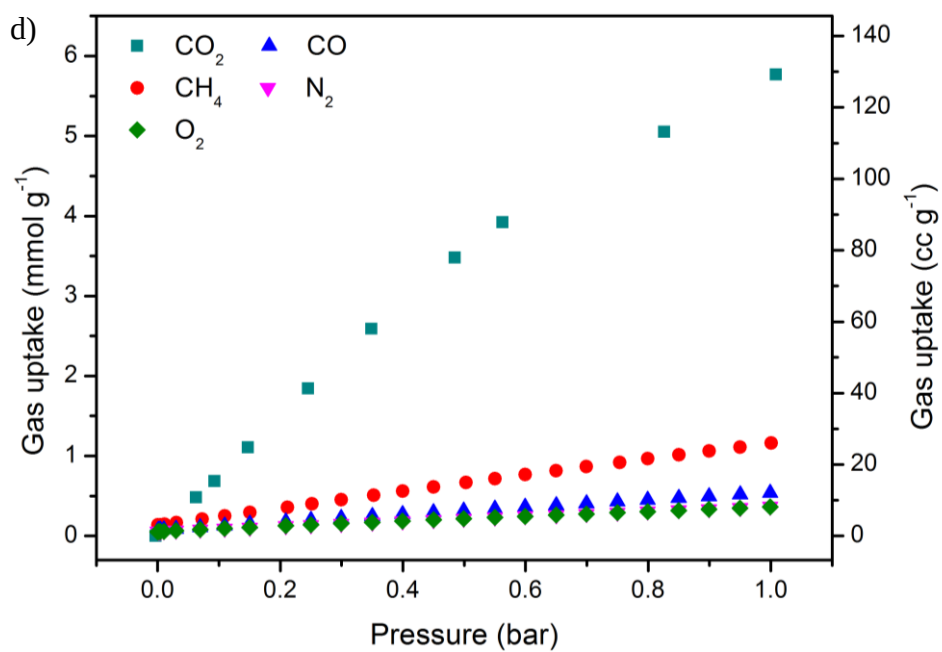
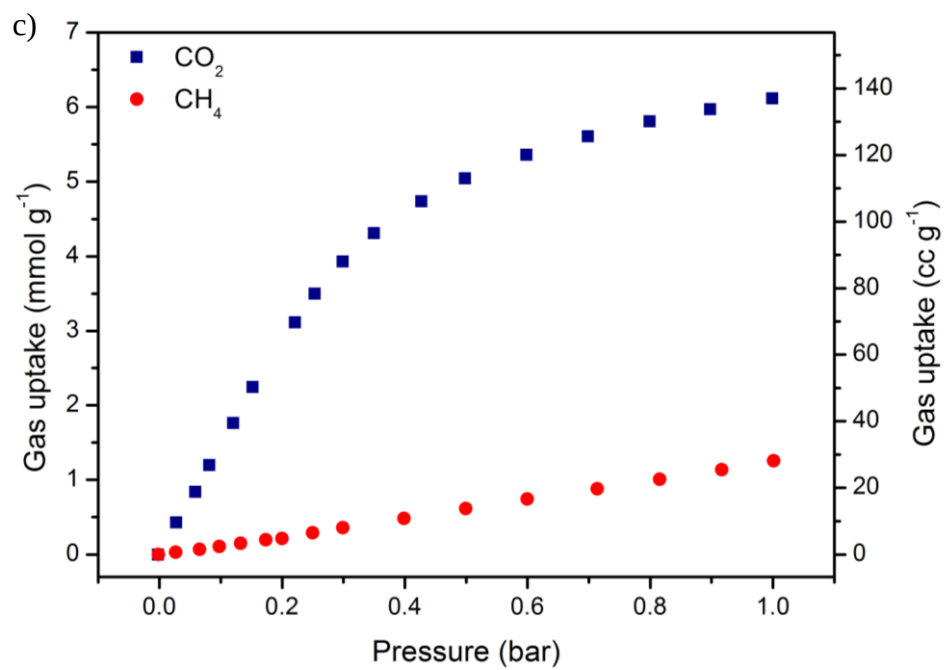
Table 3.7 – The recorded CH₄ uptake for NOTT-300(Al), NOTT-300(Cr), AlCr1:1 and [Al+Cr] at 20 bar.

3.2.4.6 CO₂ Selectivity

The selectivity of the two NOTT-300 single metal MOFs is highly affected by their difference in uptakes which in turn is affected by the differences in pore size and electronics of the –OH group. NOTT-300(Al) displays excellent CO₂ selectivity (CO₂/N₂, CO₂/CH₄, CO₂/CO); however the CO₂ selectivity of NOTT-300(Cr) is reduced as the uptakes for all gases (CO₂, CH₄ *etc.*) are higher. It has been shown that a variation in cation content has an effect on the CO₂ uptake and adsorption capacity of other gases ie CH₄. It is therefore reasonable to assume this variation then in turn affects the CO₂ selectivity and there may be potential for selectivity to be “controlled” by tuning the properties of the MOF. At all recorded temperatures AlCr2:1 displayed higher CO₂ uptakes, however, this does not mean that AlCr2:1 displays the highest selectivity as found with NOTT-300(Cr). The adsorption of CH₄ varies more greatly along the ratio series, especially as a function of temperature.

At all temperatures (273 – 303 K) the frameworks show higher adsorption capacities for CO₂, indicating all materials possess CO₂ selectivity. The CH₄ capacity is the second highest and only small amounts of N₂/CO/O₂ being adsorbed at these temperatures.





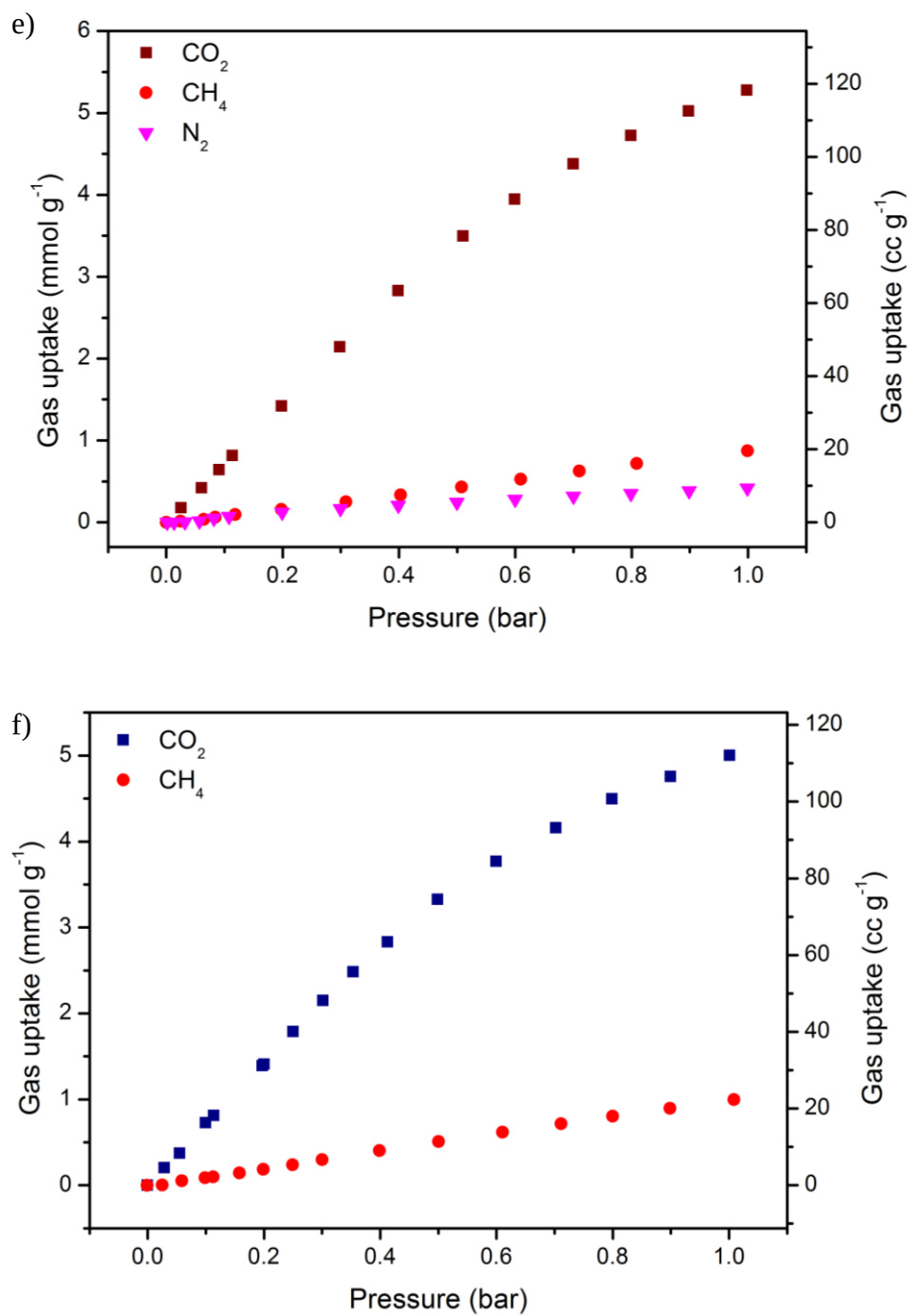


Fig. 3.21 All gas adsorption isotherms recorded from 0 – 1 bar for **a)** AlCr2:1 at 273 K, **b)** AlCr1:1 at 273 K, **c)** AlCr2:3 at 273 K, **d)** AlCr2:1 at 293 K, **e)** AlCr1:1 at 293K, **f)** AlCr2:3 at 293 K.

Selectivity		AlCr2:1		AlCr1:1		AlCr2:3	
		Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST
CO ₂ /CH ₄	273 K	10	19	15	18	12	16
	283 K	8	16	12	13	10	13
	293 K	7	9	9	10	7	9
	303 K	6	6	6	7	2	3
CO ₂ /N ₂	273 K	34	51	24	144		
	283 K	26	54	21	105		
	293 K	22	36	19	43		
	303 K	17	32	14	60		

Table 3.8 – Calculated CO₂/CH₄ and CO₂/N₂ selectivities for AlCr2:1, AlCr1:1 and AlCr2:3.

		Ratio of isotherm slopes	IAST
CO ₂ /CO	273 K	21	32
	283 K	18	27
	293 K	16	23
	303 K	11	22
CO ₂ /O ₂	273 K	34	50
	283 K	28	48
	293 K	20	38
	303 K	19	27

Table 3.9 – Calculated CO₂/CO and CO₂/O₂ selectivities for AlCr2:1.

Calculated selectivity appears to follow a general trend of CO₂/N₂ > CO₂/O₂ > CO₂/CO > CO₂/CH₄ (where applicable) for all AlCr ratios. However, each materials separation capability varied with temperature. For CO₂/CH₄ mixtures it appears AlCr2:1 has the best selectivity, as calculated by IAST, at 273 K (19 vs. 18(1:1) vs. 16(2:3)) and 283 K. After further increase in temperature to 293 K and 303 K AlCr1:1 displays higher CO₂/CH₄ selectivity. These changes in selectivity are due to the differing CH₄ adsorption observed in these materials. This changing selectivity as a function of temperature allows for the possibility of choosing a suitable material for a separation based on what temperature the separation is carried out. For example, for CO₂/CH₄ separations at 273 K

AlCr2:1 displays the highest selectivity but at higher temperatures (293/303 K) AlCr1:1 has higher selectivity.

IAST selectivity is a more effective tool for comparing gases with more similar uptakes, *i.e.* CO₂/CH₄. It becomes problematic when estimating selectivity of two very different gases such as CO₂/N₂. The theory/calculation estimates what pressure would be needed for the uptake of N₂ to be equal to CO₂ at pressure X. The uptake of N₂ will never reach the uptake of CO₂ at attainable pressures. IAST can still be used in conjunction with other methods to predict the selectivity, however when using the theory to estimate uptake of binary mixes, it over exaggerates CO₂ contribution. For CO₂/N₂ selectivity IAST clearly shows AlCr1:1 has the highest selectivity, however, the selectivity calculated from the isotherm slopes shows that AlCr2:1 has the highest CO₂/N₂ selectivity at all temperatures. Both methods have drawbacks, especially when using this mixture of gases. Comparison of N₂ uptakes under these conditions (273 – 303 K and 0 – 1 bar) shows that AlCr2:1 should have highest CO₂/N₂ selectivity, as the uptakes of N₂ are lower, and uptakes of CO₂ are higher. However, when the techniques are both applied together a general idea for gas selectivity can be obtained.

In general, all ratios experience a reduction in selectivity when temperature is increased. Possibly due to the faster kinetics of the gases inside the channel, diffusion is less hindered at these higher temperatures and the H-bonds between more easily adsorbed gas (CO₂) and framework are more easily broken. In nearly all cases explored the mixed metal MOFs display higher CO₂ selectivity than NOTT-300(Cr). The most obvious exception is CO₂/CO, where Cr has higher selectivity at 273 K and at all other temperatures the selectivity is comparable.

However, the reported CO₂ selectivity of NOTT-300(Al) is higher than all Cr containing analogues, by a significant amount. The Cr containing analogues, (NOTT-300(Cr) and all NOTT-300AlCr_s) exhibit much higher adsorption capacity for CO₂ and still possess good CO₂ selectivity. So, although NOTT-300(Al) may have higher selectivity the overall CO₂ uptake is lower. Variation of cation content present in the sample clearly affects the materials CO₂ adsorption and selectivity. There is no observable trend in CO₂ selectivity when viewed as a function of amount of Cr present. So although the option to choose an appropriate material for the required separation process based on the temperature at which this process takes place is possible, the possibility for predictive design will be difficult. It is clear from this that the amount of each metal present in the framework structure has an affect on the CO₂ adsorption and selectivity. However, there also appears to be no discernible trend with respect to amount of each -OH group present either and so further investigation into this series is required.

3.2.4.7 Dual Component CO₂ Adsorption Isotherms in NOTT-300AlCr₂:1

A series of dual component adsorption isotherms (CO₂/CH₄, CO₂/CO and CO₂/N₂) were carried out on NOTT-300AlCr₂:1 in order to assess how the presence of other gases affect the CO₂ uptake and therefore give us insight into the CO₂ selectivity of this material.

The CO₂/CH₄ (1:1) dual component adsorption reaches a total uptake of 15.99 wt% at 293 K and 1 bar. The corresponding uptakes of CO₂ and CH₄ are 15.39 and 1.06 wt% respectively at 0.5 bar. IAST predictions follow closely with the experimental adsorption, giving a total uptake of 16.01 wt% at 1 bar, clearly

showing the reliability of the IAST model in this case. The high wt% adsorbed in the dual component isotherm is indicative of high CO₂ adsorption, as increased CH₄ adsorption would lead to a decrease in wt%, since CH₄ is lighter than CO₂ per molecule.

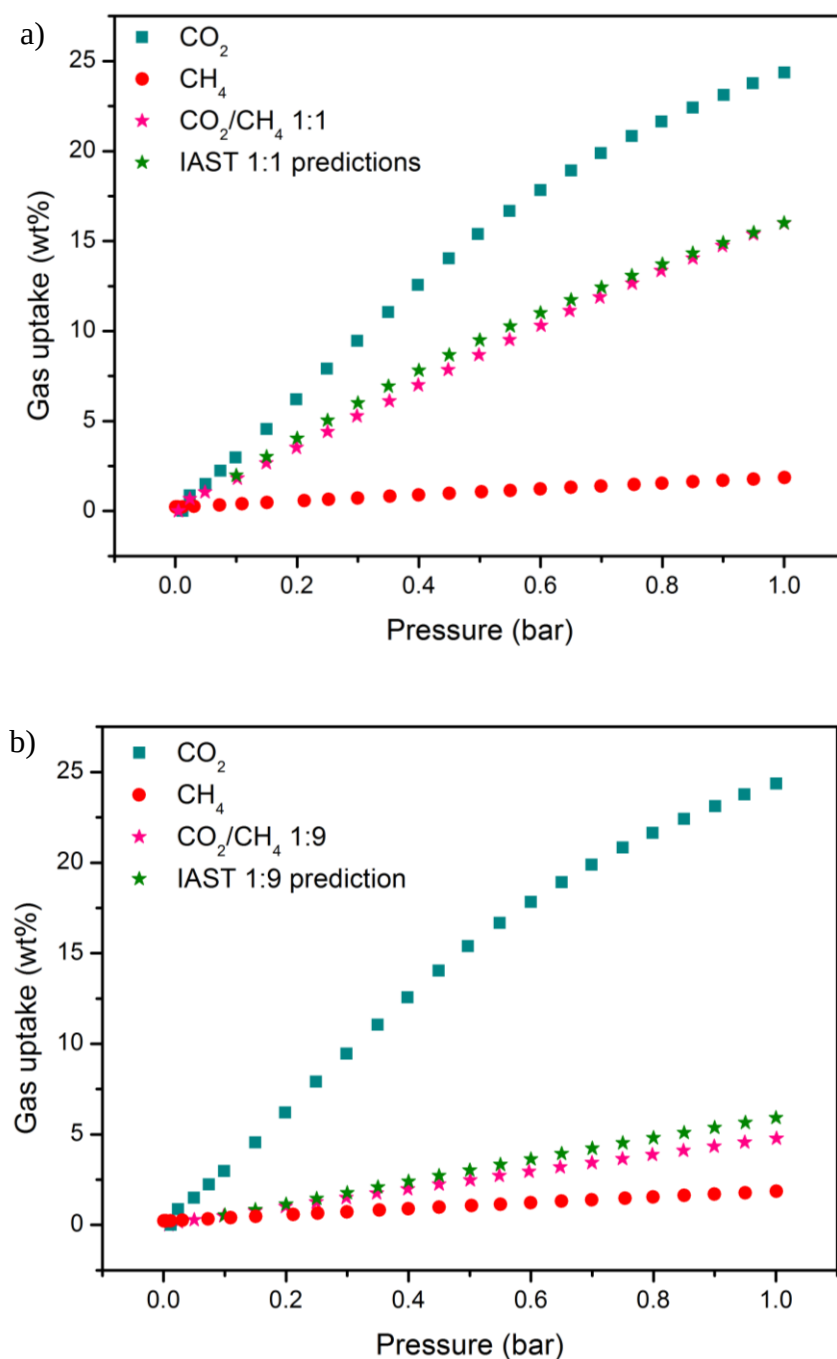


Fig. 3.21 Dual component adsorption isotherm carried out for NOTT-300(AlCr₂:1) from 0 – 1 bar for CO₂/CH₄ **a)** 1:1 **b)** 1:9 mixture at 293 K.

A lower concentration of CO_2 present (1:9 $\text{CO}_2:\text{CH}_4$) leads to a larger discrepancy between the IAST predicted uptake and the experimental adsorption, 5.90 wt% and 4.78 wt% respectively at 293 K and 1 bar. The CO_2 adsorption at low pressure (0.1 bar) reaches 2.97 wt%. Owing to the increased presence of CH_4 an increased uptake of CH_4 compared with the 1:1 (CO_2/CH_4) experiment is not unreasonable to assume, however, the shape of the isotherm clearly indicates high CO_2 adsorption. As the mix is 90% CH_4 you would expect the isotherm to match the single component CH_4 adsorption isotherm if a high amount of CH_4 is adsorbed. The differences in uptake between CO_2 and CH_4 can be easily explained by considering the dipole/quadrupole moment of CO_2 . CO_2 possesses a large quadrupole moment, able to interact with -OH group electrostatically, however CH_4 has no permanent dipole or quadrupole moment and so cannot form these interactions with the framework.

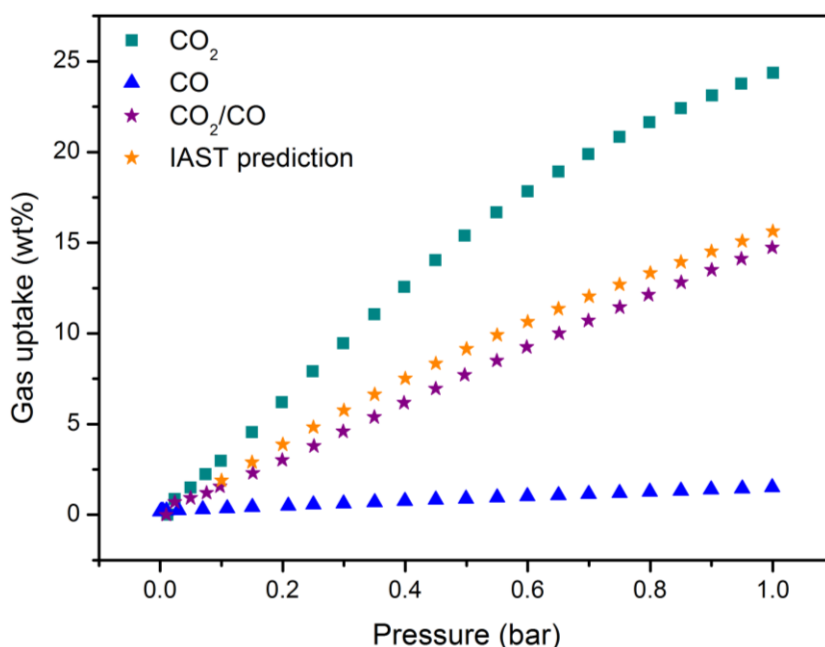


Fig. 3.22 Dual component adsorption isotherm carried out for $\text{AlCr}_2:1$ from 0 – 1 bar for a CO_2/CO 1:1 mixture at 293 K.

CO is often present in small amounts in common CO₂ separations, such as post combustion CO₂ capture. Flue gas is known to contain several contaminants such as CO. The CO₂/CO flow adsorption isotherm reaches a total uptake of 14.74 wt% at 293 K and 1 bar. This total uptake is similar to that achieved in pure component CO₂ adsorption at 0.5 bar, 14.03 wt%. CO adsorption under these conditions is low, only reaching 0.89 wt%. The IAST prediction matches the experimental adsorption relatively closely but possibly over predicts the CO₂ contribution to the overall uptake owing to the large difference in CO₂ and CO uptakes at this temperature and pressure.

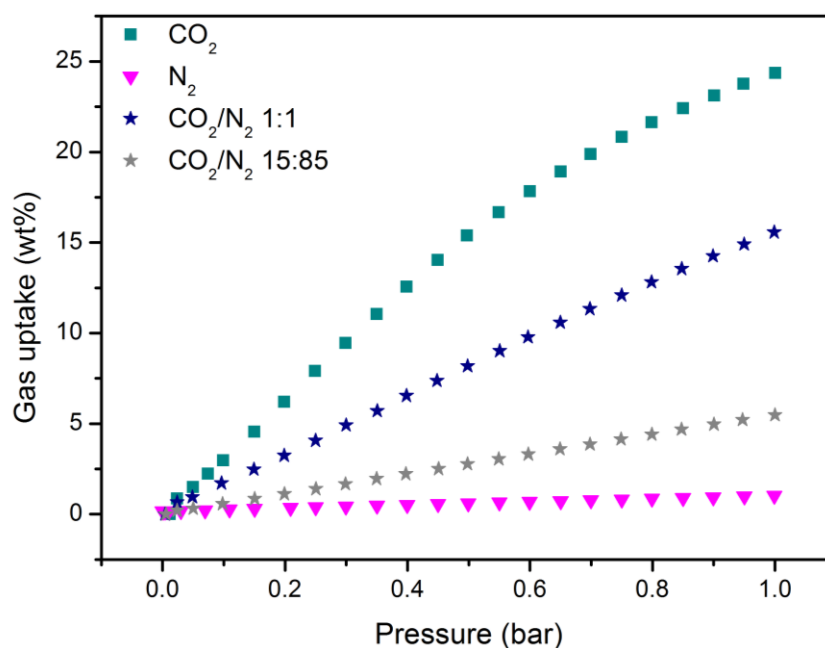


Fig. 3.23 Dual component adsorption isotherm carried out for AlCr2:1 from 0 – 1 bar for CO₂/N₂ mixtures at 293 K.

For CO₂/N₂ mixtures IAST predictions become too unreliable and the predictions closely follow the pure CO₂ isotherm as the difference in adsorption is too large for this theory to successfully be applied. Dual component adsorption isotherms still give insight into selectivity, better than IAST can. A 1:1 mixture of N₂ and CO₂ reaches a total uptake of 15.57 wt% at 293 K and 1 bar. This

uptake is very close to the pure CO₂ uptake up to 0.5 bar, 15.39 wt%, with the corresponding N₂ adsorption only reaching 0.60 wt% at 0.5 bar. This clearly shows that the presence of N₂ does not affect the CO₂ adsorption significantly as high CO₂ adsorption is still achieved. At lower concentrations of CO₂ (15 %) the overall uptake is lower, reaching 5.48 wt% at 293 K and 1 bar. This concentration of gases was chosen due to the close relation to the conditions of flue gas; a large amount of N₂ and low partial pressures of CO₂. At this low pressure (0.15 bar) the CO₂ uptake is 4.55 wt%, which is lower than the experimental uptake recorded for the dual component adsorption. However, the shape of the dual component isotherm (15:85) is a clear indication that majority adsorbed gas is CO₂. The adsorption is shallower which is expected due to the low concentration of CO₂, however, it is still steeper than pure N₂ isotherm. Clearly showing only small amounts, if any, N₂ is adsorbed.

3.2.5 CO₂-Loaded *In Situ* Synchrotron PXRD

As with NOTT-300(Al) and NOTT-300(Cr), NOTT-300AlCr₂:1 was analysed by *in situ* CO₂ loaded PXRD to investigate how the mixing of cations affects the CO₂ interactions with the framework. As the different –OH groups present in the sample are expected to interact with CO₂ differently; this has already been shown in Chapter 2 with the interaction between the adsorbed CO₂ and the bridging -OH group differing in strength depending on the metal present. CO₂ forms stronger interactions with the -OH in NOTT-300(Al) than in NOTT-300(Cr).

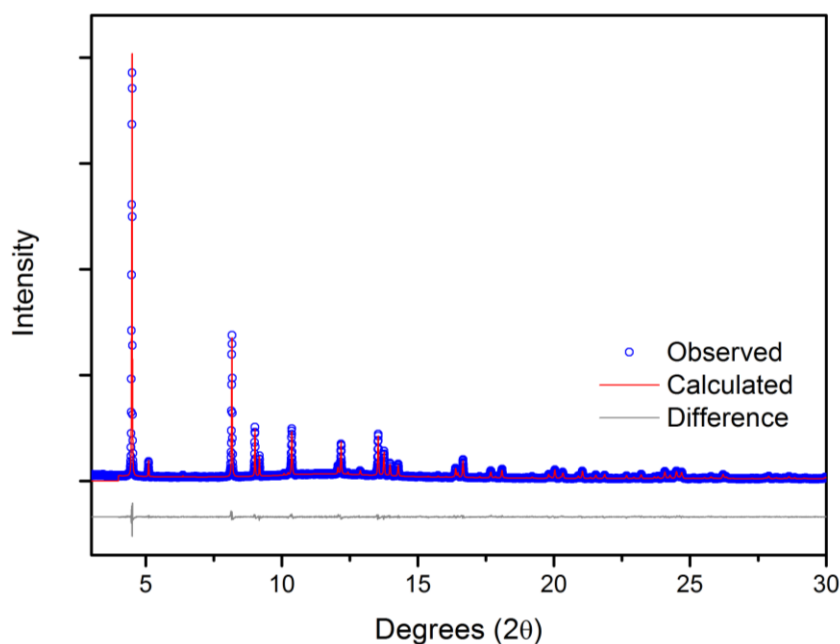
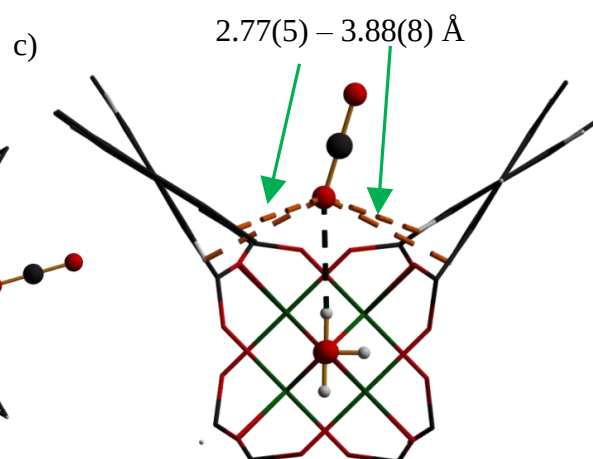
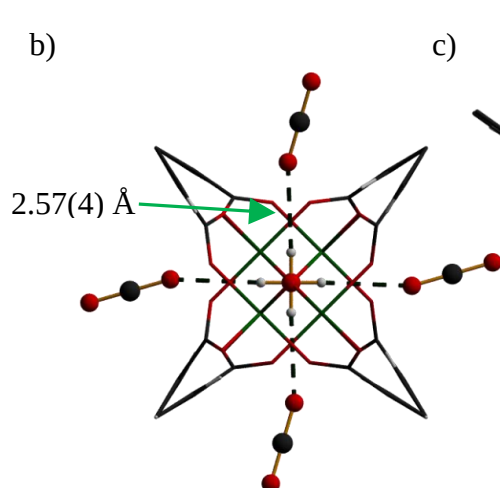
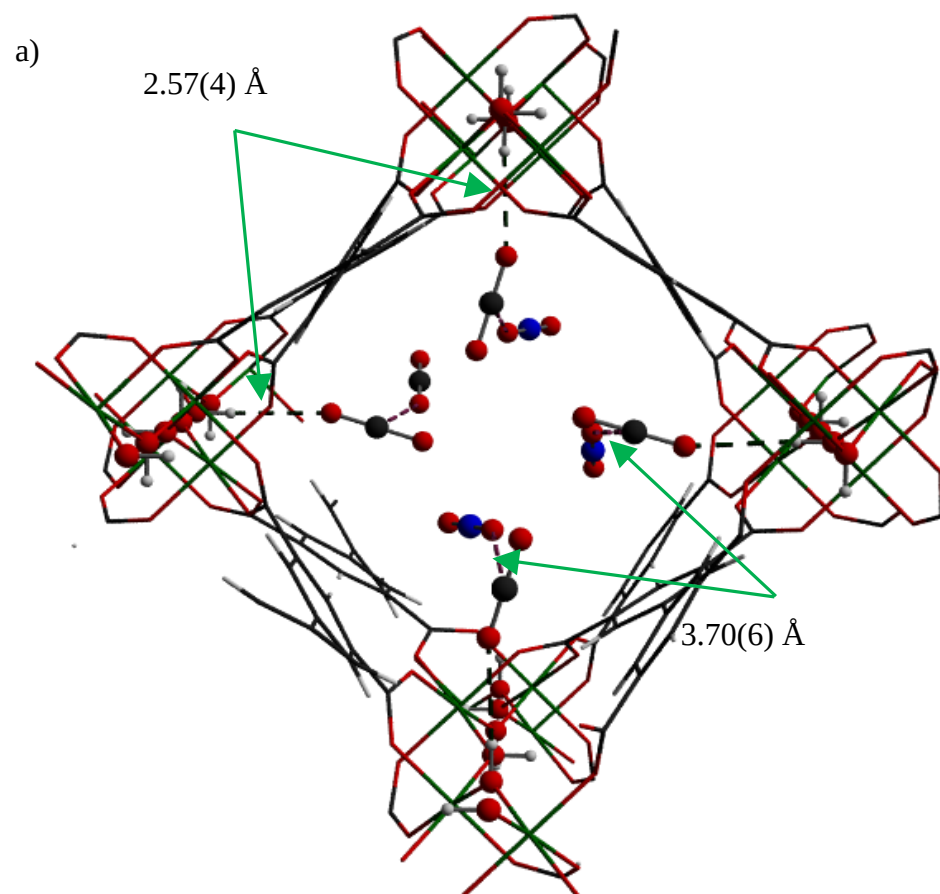


Fig. 3.24 PXRD patterns [observed (blue), calculated (red) and difference (grey)] for the Rietveld refinement of CO₂ loaded NOTT-300AlCr₂:1 λ - 0.825633.

There were two distinct CO₂ adsorption sites found within NOTT-300AlCr₂:1, CO₂(I) and CO₂(II). CO₂(I) interacts predominantly with the framework through a H-bond with the bridging –OH group with a OH...OCO distance of 2.57(4) Å. Again the CO₂ molecules exhibit positional disorder owing to the location of the adsorption site and as such the occupancy of each site is ~ 0.5. This equates to approximately one CO₂ per –OH group which is consistent with the adsorption recorded at 1 bar. One drawback using PXRD with this mixed metal material is that it is not able to distinguish between the two metal centres, and therefore all distances given are an average of those found in the whole sample. There is no separation of Al-(OH)-Al, Cr-(OH)-Cr or Al-(OH)-Cr. This interaction between –OH and CO₂(I) is not completely linear, with a H-O....C bend of 161°. This CO₂ adsorption site is further supported by collective weak van der Waals interactions from the aromatic hydrogens on the phenyl ring of the adjacent

biphenyl ligands. These weaker interactions range from 2.77(5) – 3.88(8) Å. The second CO₂ site located within the pore interacts predominantly with the first CO₂ molecule through a dipole interaction with a distance of 3.70(6) Å. The two CO₂ molecules interact in a bent T-shape, with an angle of 153.5° (< O---C=O). This CO₂(II) position is also reinforced by collective weak van der Waals interactions from the aromatic hydrogens.



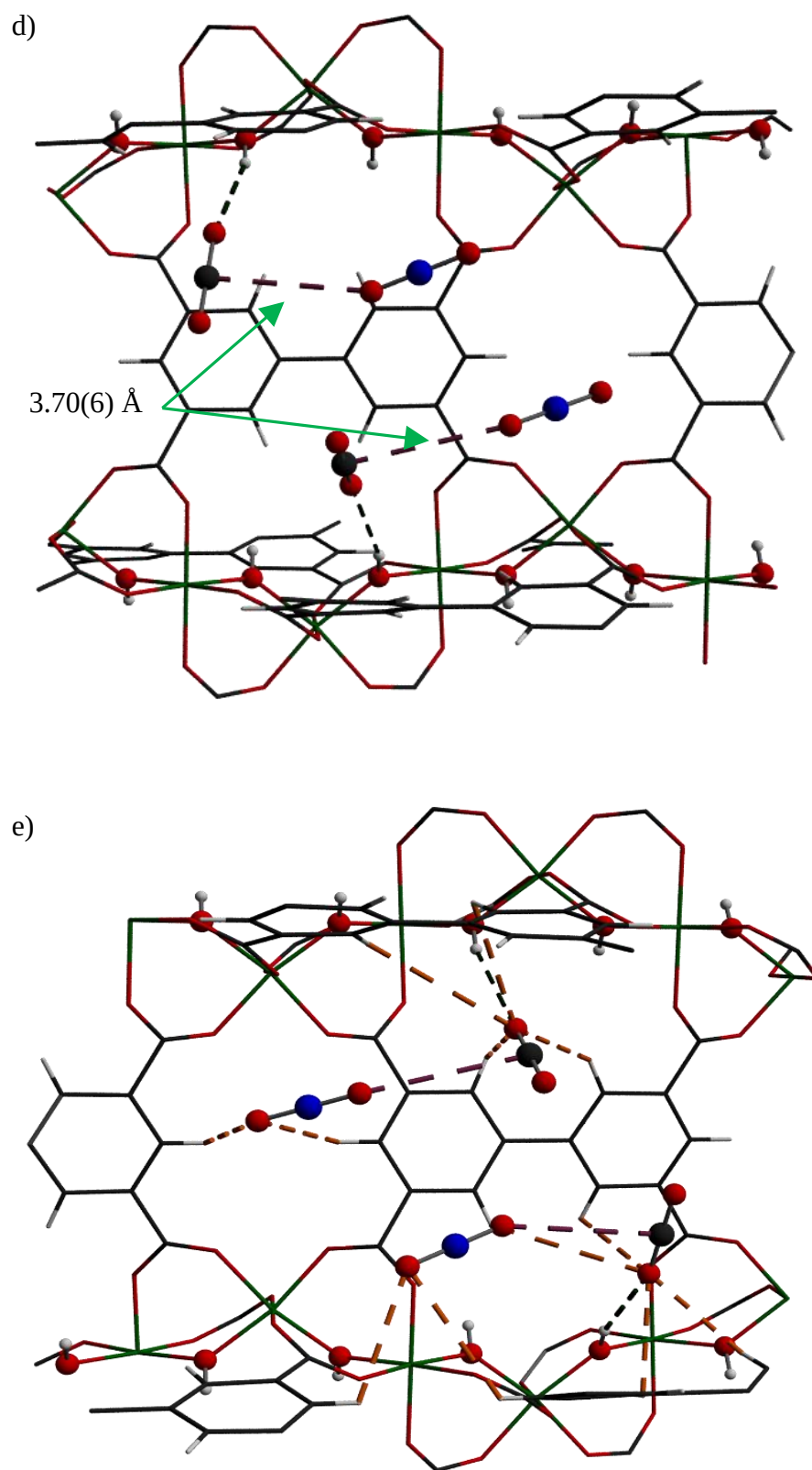


Fig. 3.25 Views of the structure of CO₂ loaded NOTT-300AlCr obtained from PXRD with the disorder removed for clarity. (AlCr – green, oxygen – red, carbon – grey, hydrogen – white) **a)** View of adsorbed CO₂ in the pore channel. The adsorbed CO₂ molecules and μ_2 -OH groups are

highlighted in ball and stick mode. The carbon atom of CO₂ (II) is highlighted in blue. The H-bonds between O(δ^-) of CO₂ and H(δ^+) from the –OH group is highlighted in green, [O $\cdots$ H = 2.57(4) Å], dipole interactions between CO₂ (I) and (II) are highlighted in purple [O=C=O $\cdots$ CO₂ = 3.70(6) Å] and van der Waals interactions between aromatic hydrogens and CO₂ (I) and (II) are highlighted in orange [O $\cdots$ H = 2.77(5) – 3.88(8) Å]. **b)** Detailed view of O–H $\cdots$ OCO H-bonds and the bent angle of interaction, the <OH $\cdots$ O bond angle is 161°. **c)** View of cooperative/assistive van der Waals interactions between aromatic hydrogens and CO₂ (I). **d)** CO₂ (I) and CO₂ (II) dipole interaction and packing in the channel. **e)** Detailed view of CO₂ (I) and CO₂ (II) dipole interaction and additional van der Waals interactions between adsorbed gas and framework (distances not included for clarity). The C–O bond distances in CO₂ are 1.17(8) (CO₂(I)) and 1.15(3) Å (CO₂(II)).

NOTT-300AlCr₂:1 does display a combination of NOTT-300(Al) and NOTT-300(Cr) properties to some extent, with differences arising due to the presence of the Al–(OH)–Cr moiety. The H-bond between CO₂(I) and –OH is longer in AlCr than both NOTT-300(Al) and NOTT-300(Cr), indicating that overall the CO₂ interaction with the framework is weaker in AlCr than in both single metal MOFs. However, the CO₂(I)–CO₂(II) distance in AlCr is shorter than that found for NOTT-300(Al), meaning a stronger interaction between the two CO₂ molecules in the mixed metal material. This is reflected in the CO₂ uptake of the two materials, with AlCr reaching higher CO₂ adsorption than both NOTT-300(Al) and NOTT-300(Cr) at higher pressures where these CO₂–CO₂ interactions play a predominant role in uptake. However, these interactions are shorter in NOTT-300(Cr) showing that of the three MOFs, Cr has the strongest CO₂–CO₂ interactions and also displays the highest CO₂ uptakes at high pressures, as well as a higher heat of adsorption at high loadings of CO₂. At lower pressures, where the –OH–OCO interaction is most dominant, the uptake of CO₂ for AlCr, closely follows the adsorption of Cr, with Al reaching higher

uptakes more rapidly. Again this is shown nicely by the numbers as Al has shortest OH-CO₂ H bond and AlCr and Cr both have similar H bonds, although AlCr is longest. It is not possible to distinguish between the different –OH groups present (Al-Al, Cr-Cr and Al-Cr) using PXRD and so cannot monitor how each one behaves in presence of CO₂, instead an overall average is given, which still provides useful insights into interactions and the behaviour of CO₂ adsorbed in this material.

3.2.6 CO₂-Loaded *In Situ* IR for NOTT-300AlCr₂:1

In situ CO₂ loaded IR provides the unique ability to be able to monitor how each -OH group is affected by the presence of CO₂. The activated spectra were collected after each sample had been heated under vacuum and all solvent molecules removed, as presence of H₂O would overlap significantly with the $\nu(\text{OH})$ stretch region of the spectrum. The spectrum displays three peaks in the significantly with the $\nu(\text{OH})$ stretch region, 3692 cm⁻¹, 3673 cm⁻¹ and 3645 cm⁻¹. When overlapping the spectrum of the mixed metal material with both single metal spectra, clear alignment of two of the peaks is observed and they can be attributed to Al-(OH)-Al (3691 cm⁻¹) and Cr-(OH)-Cr (3645 cm⁻¹). The third observed peak lies between the two single metal –OH peaks and we assign this to $\nu(\text{OH})$ of an –OH shared by both Al and Cr. This clearly demonstrates how the metal centres either side of the bridging –OH group affect the electronic properties of OH. It is not known if there are longer range interactions occurring within the framework, *i.e.* that the nature of the second nearest metal cation also has an influence on the –OH bonding and potentially on the interaction with

guest gas molecules such as CO₂, although it is not unreasonable to assume this is the case.

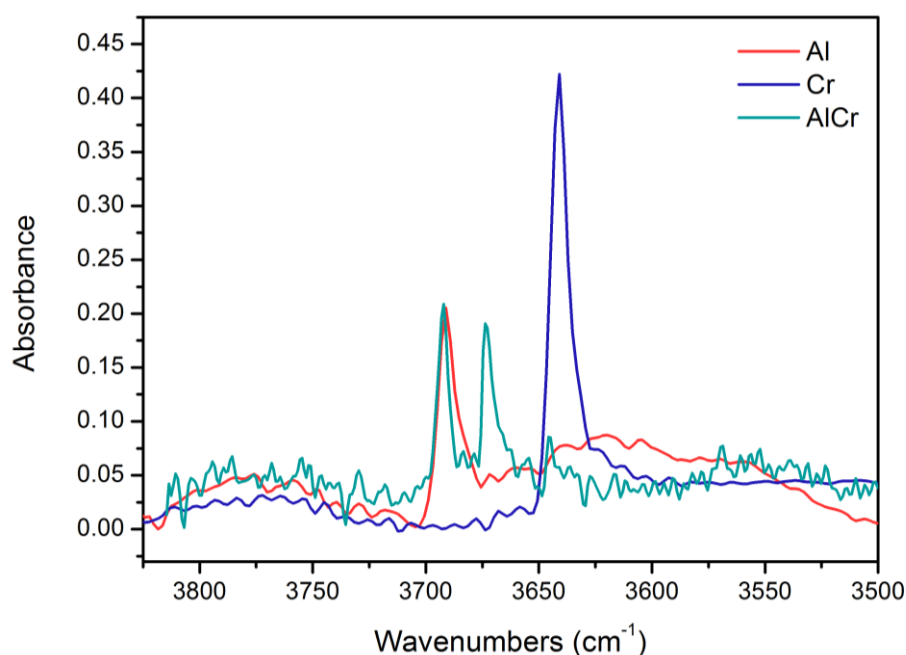


Fig. 3.26 IR spectra for NOTT-300(Al) (red), NOTT-300(Cr) (blue) and NOTT-300(AlCr₂:1) (teal).

The introduction of CO₂, from 0 – 1 bar in 0.2 bar intervals, appears to affect all three peaks by differing amounts. The $\nu(\text{OH})$ peak attributed to Cr-(OH)-Cr does not appear to shift significantly at any concentration of CO₂. As discussed in section 3.3.5 this moiety interacts weakly with CO₂ and so this is not unreasonable, but a small shift was still expected. The peak shape itself however does appear to broaden on introduction of CO₂, indicating some change is occurring, possibly a combination of two unresolved peaks in one broad peak corresponding to -OH and -OH-OCO. The $\nu(\text{OH})$ peak attributed to Al-(OH)-Al appears to shift the most from as CO₂ concentration is increased, indicating a stronger interaction with CO₂, and full occupation of the adsorption site adjacent to the -OH. This is supported by the single metal NOTT-300(Al) PXRD, which

shows the shortest –OH-OCO distance. The $\nu(\text{OH})$ assigned to the –OH bridging the two different metal centres also shifts significantly with increasing CO_2 concentration. As the $\nu(\text{OH})$ stretch for both Al-(OH)-Al and Al-(OH)-Cr shift a lot with CO_2 , (10 cm^{-1} and $\sim 6\text{ cm}^{-1}$, respectively) it is likely that both –OH groups form relatively strong H bonds with CO_2 , stronger than that found between CO_2 and Cr-(OH)-Cr. The presence of the weaker Cr-(OH)-Cr CO_2 interaction will contribute to the longer H-bond seen in the PXRD data.

	$\nu(\text{OH})\text{ (cm}^{-1}\text{)}$	$\nu(\text{OH})\text{ (OH+CO}_2\text{)}\text{ (cm}^{-1}\text{)}$
Al-OH-Al	3691.6	3683.4
Al-OH-Cr	3672.0	3665.7
Cr-OH-Cr	3645.1	3644.8

Table 3.10 Peak position of the different $\nu(\text{OH})$ stretches present in the IR spectra of NOTT-300(AlCr_2 :1)

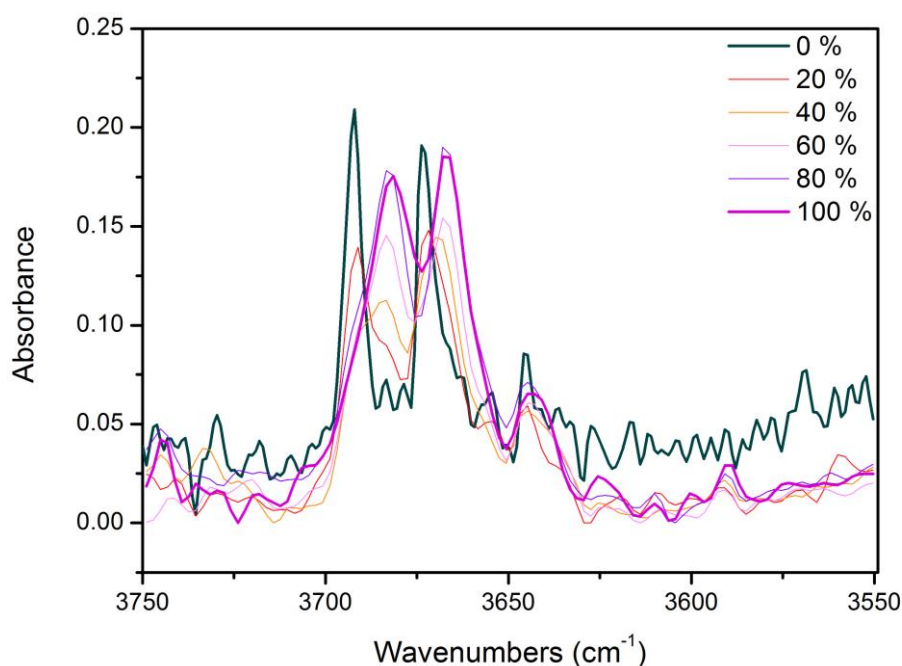
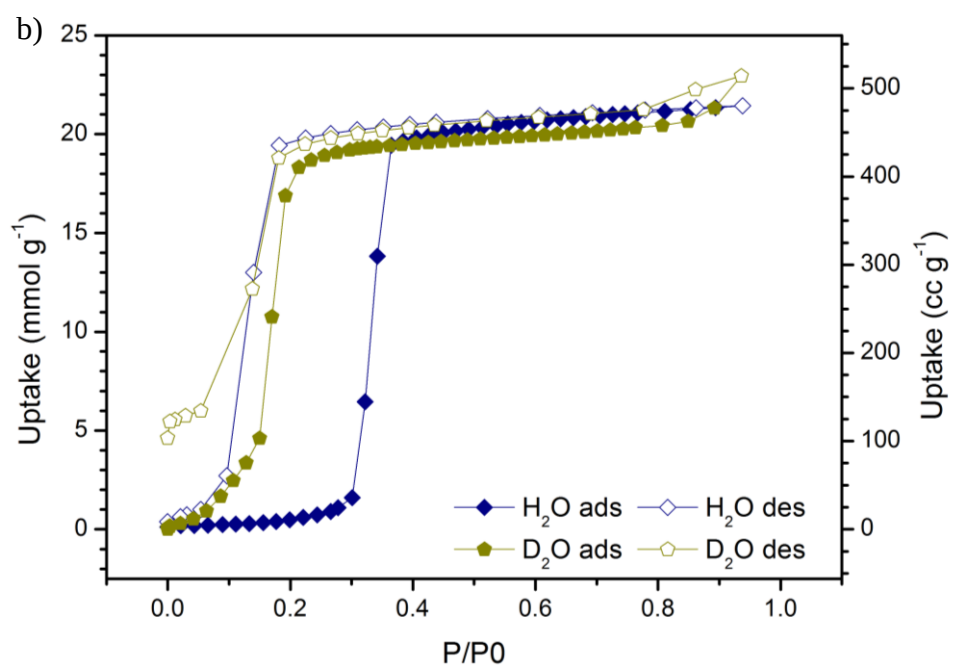
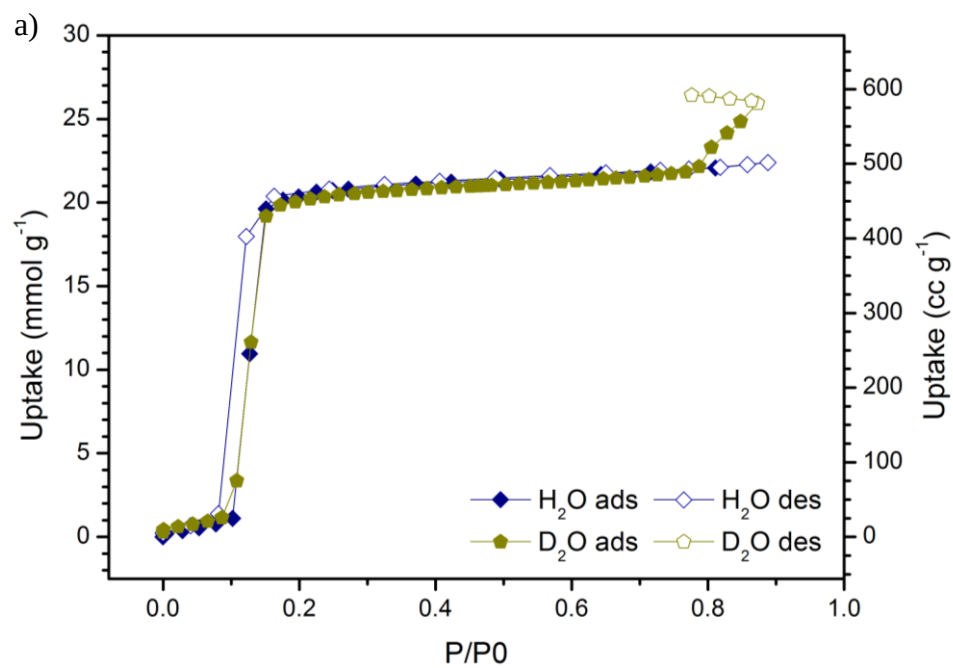


Fig. 3.27 IR spectra showing behaviour of $\nu(\text{OH})$ stretch in $0 \rightarrow 100\%$ CO_2 for NOTT-300(AlCr_2 :1).

3.2.7 Water and Heavy Water Vapour Adsorption in NOTT-300(AlCr₂:1)

A series of water vapour adsorption isotherms were carried out, as stability to water vapour is crucial for solid adsorbents to be considered for CO₂ separation applications, such as post combustion capture, as water vapour is present in the mixture of gases. A series of heavy water (D₂O) vapour adsorption isotherms were also carried out in order to see if there were any differences and to investigate possible selectivity/separation.

At 283 K the adsorption of both vapours is very similar, in both uptake values and isotherm shape. The adsorption for both vapours appears to occur in a step-wise fashion, with the majority of adsorption taking place above 0.15 P/P₀ for both vapours, saturation is reached extremely quickly and a plateau is maintained for the rest of the increase in pressure. However, for D₂O there appears to be another sharp increase in adsorption above 0.8 P/P₀ and the desorption appears to show the beginning of a hysteresis, before the instrument broke and the measurement could not be completed. There is also a slight hysteresis upon desorption for H₂O, however, the adsorption is fully reversible as total reduction in pressure removes all adsorbed H₂O.



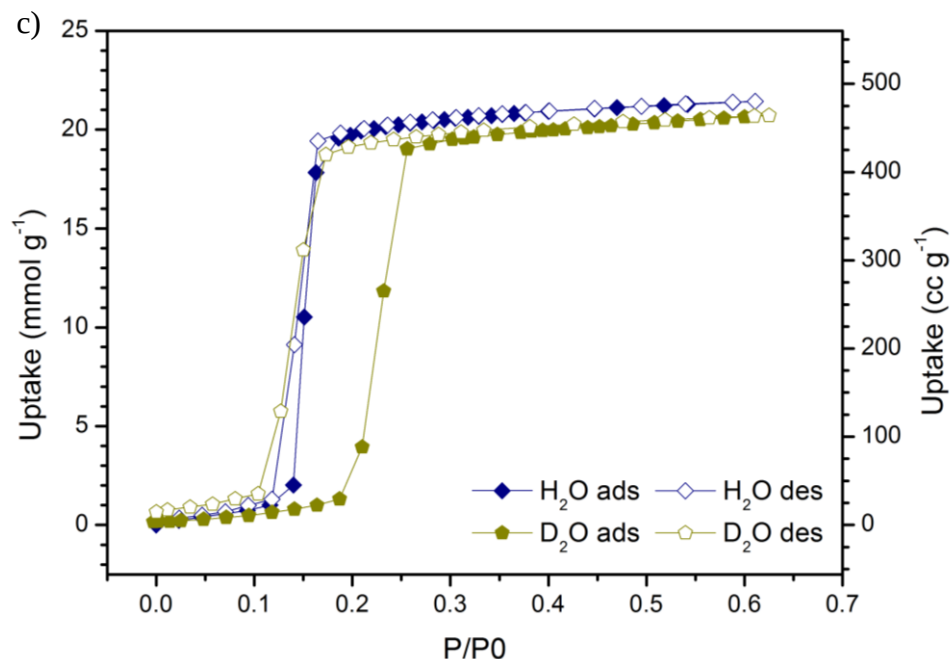


Fig. 3.28 H₂O and D₂O vapour adsorption isotherms for NOTT-300AlCr₂:1 carried out at **a)** 283 K, **b)** 293 K and **c)** 303 K.

The differences in adsorption behaviour of the two vapours become more apparent at 293 K and 303 K, with potential for selective adsorption of D₂O and H₂O respectively. At 293 K the adsorption is different for the two vapours; with adsorption of D₂O occurring instantly but gradually until 0.2 P/P₀ after which the uptake increases rapidly and saturation is reached. H₂O only starts adsorbing above 0.3 P/P₀, with rapid uptake occurring after 0.35 P/P₀. Both display a large hysteresis upon desorption, but only full removal of H₂O is achieved with some D₂O remaining in the sample on full desorption. This shows that AlCr₂:1 can selectively adsorb D₂O over H₂O at this temperature as the adsorption begins at different P/P₀.

At 303 K the potential to selectively adsorb H₂O is seen, as the step-wise adsorption for H₂O occurs at lower P/P₀ than for D₂O, 0.15 P/P₀ and 0.2 P/P₀ respectively. Another difference between the two vapours under these conditions

is the behaviour of the desorption, with D₂O displaying large hysteresis whereas H₂O desorption closely follows the adsorption.

The separation capability of this material is not retained at 313 K, with both vapours displaying similar adsorption and desorption behaviours.

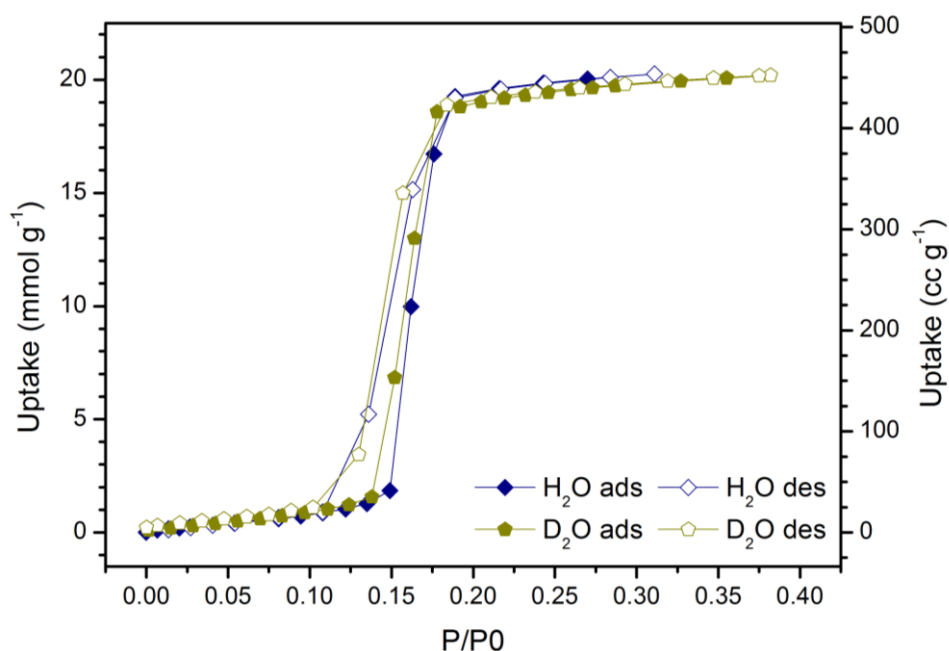


Fig. 3.29 H₂O and D₂O vapour adsorption isotherm carried out at 313 K.

The high uptakes of both H₂O and D₂O shows the material has a high stability in the presence of water vapour. However, this high adsorption could prove problematic for CO₂ separation when water vapour is present, as the water could competitively bind to the framework. Therefore the CO₂ adsorption and selectivity could be diminished by presence of water vapour. This can be further probed by running “wet” gas adsorption isotherms, where the gas stream has an amount of water vapour present, this could provide valuable insights.

3.3 Conclusion and Summary

A series of Al and Cr mixed metal MOFs analogous to NOTT-300 have been successfully synthesised with varying amounts of each metal present, 2:1, 1:1 and 2:3. The distribution of these metals throughout the framework were shown to be homogeneous on the atomic level by IR, *i.e.* the samples are not simple mechanical mixtures of the two pure metal crystallites. Varying the cation content appears to only have small effects on structural properties of NOTT-300. Owing to the similar sizes of Al and Cr, only small changes in unit cell are expected. Other properties, such as thermal stability and gas adsorption behaviour appear to be affected much more by the variation in cation content. There is not always a trend in these properties when considering as a function of metal content, *i.e.* more Cr does not automatically mean more thermally stable or higher CO₂ uptake. The properties displayed by these mixed materials appear to be unique to the material and not merely a combination of single metal MOF characteristics. The differences in gas uptakes in turn lead to differences in gas selectivity across the range of materials. This gives the ability to choose an ideal material for a specific application based on the conditions of the separation process, *i.e.* AlCr₂:1 shows better CO₂/CH₄ selectivity at 273 K but at 293 K AlCr₁:1 has the highest selectivity.

All mixed metal MOFS show high CO₂ uptake and good CO₂ selectivity.

In situ CO₂ loaded PXRD data shows high CO₂ adsorption observed in AlCr₂:1 is in part due to H-bonds between CO₂ and the bridging -OH groups, further reinforced by weak van der Waals from aromatic hydrogens. These are the same interactions as found within both single metal NOTT-300(Al) and

NOTT-300(Cr), however, the strengths of these interactions vary with each of these samples as an effect of how the metal centre affects the –OH electronics which in turn affect the CO₂ uptake at low pressures. IR spectroscopy allows a deeper probe into this behaviour and it was found that the –OH group bridging the two Cr centres together interacts the weakest with CO₂ as the $\nu(\text{OH})$ peak barely shifts at all CO₂ concentrations, reinforced by earlier CO₂ loaded PXRD studies on the single metal NOTT-300(Cr). Both Al-(OH)-Al and Al-(OH)-Cr appear to interact with CO₂ much more strongly as a clear shift can be observed in the $\nu(\text{OH})$ band position with increasing amounts of CO₂.

It is not known if there are longer range effects taking place within the sample and if so, to what extent as it is possible to fit many peaks to the IR data. This could possibly be investigated further in the future and may yield interesting results.

H₂O/D₂O adsorption was also studied in AlCr₂:1 and it was found that separation of these two vapours is possible at 293 K and 303 K due to the steps in adsorption occurring at different pressures.

One avenue to continue this work would be to investigate the spatial distributions of the different metal centres throughout the framework. To assess how the distribution varies across the ratios and also across samples of the same ratio. This could provide useful information as the distribution of each metal will significantly affect the amount of each -OH group present which has already been shown to have an important effect on the CO₂ adsorption of the mixed metal series. This could be pursued by using EDX spectroscopy and other surface mapping techniques.

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**Chapter 4 – C₂ Hydrocarbon Adsorption in
NOTT-300 Series (Al, Cr, AlCr₂:1, AlCr₁:1
and AlCr₂:3)**

4.1 Introduction

As discussed in Chapter 1, there are many industrial processes that rely on a feedstock of small hydrocarbons, such as ethylene.¹ Hydrocarbons are mostly generated from petroleum and natural gas processing and are separated into various component fractions.^{2,3} These separation processes often have high energy costs therefore substantial research has been carried out in order to find a more energy and cost efficient method.⁴ There are two main ways in which MOFs can be used to separate hydrocarbons through selective adsorption: the first is through differences in interactions of the adsorbates with strong binding sites such as unsaturated metal centres and the second is through size selective adsorption/exclusion (sieving effects).^{5,6,7,8} There is a potential to design a MOF for a specific hydrocarbon separation by incorporating one or both of these properties.

Chen *et al.* recently reported the synthesis of a microporous MOF (MMOF), UTSA-60 [Cu₂BTAA(H₂O)₂] (H₄BTAA – benzene-1,2,4,5-tetraacrylic acid), a 3D framework consisting of Cu(II) paddlewheel units bridged by the ligand (Fig. 4.1).⁹ The framework contains three types of channel, one along each axis and the channel that runs along the *b* axis is decorated by a large number of unsaturated Cu(II) sites for interaction with adsorbed gas. UTSA-60 possesses both small pore channels and unsaturated Cu(II) sites and can thus selectively adsorb C₂H₂ over C₂H₄. The C₂H₂ uptake at 296 K and 1 bar is moderately high at 70 cc g⁻¹, which is unusual for a MMOF which suffer from low C₂H₂ adsorption capacity due to narrow pore windows. The C₂H₄ adsorption is lower, reaching an uptake of 46 cc g⁻¹ at 296 K and 1 bar, leading to an IAST calculated selectivity of 16, one of the highest selectivities reported for a MOF material.

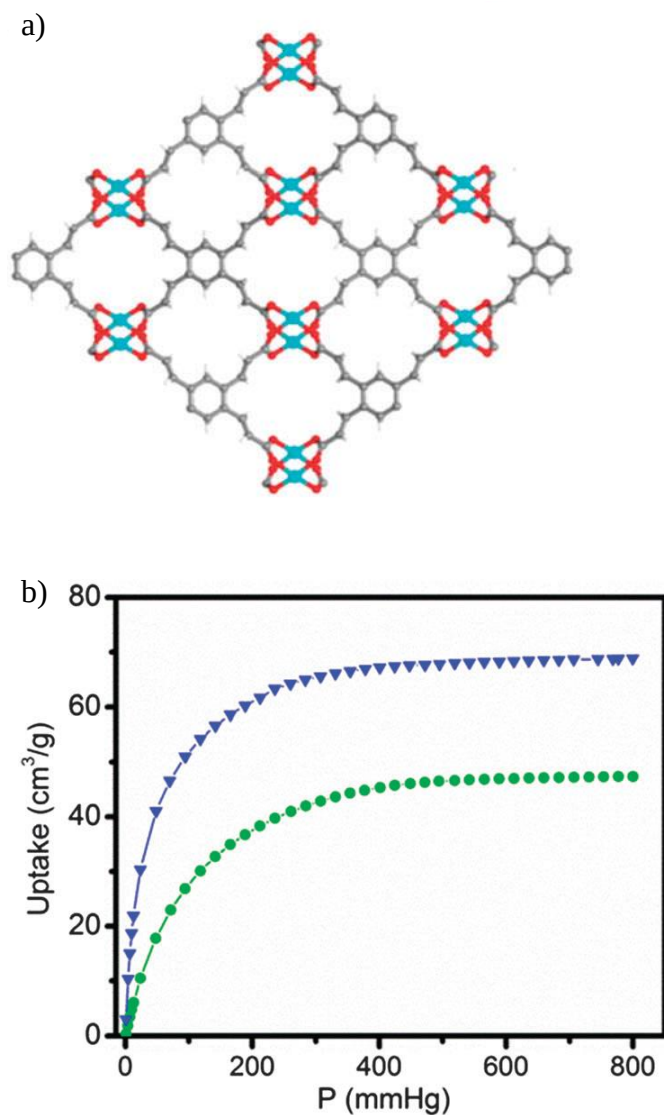
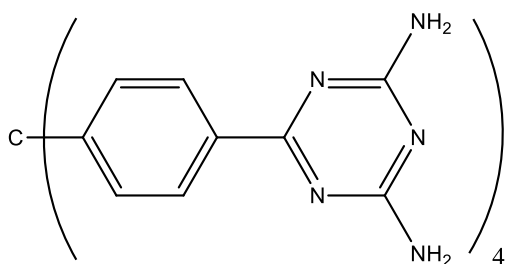


Fig. 4.1 a) View of the crystal structure of UTSA-60 **b)** C₂H₂ (blue) and C₂H₄ (green) adsorption isotherms for UTSA-60 at 296 K. Figures taken from reference 9.

Another porous molecular material that has been investigated for selective C₂H₂ adsorption is HOF-1.¹⁰ Hydrogen-bonded organic frameworks (HOFs) are similar to MOFs in that they exhibit 3D porous structures but contain no metal. Instead the framework is held in place by supramolecular interactions such as hydrogen bonds and π - π stacking interactions. HOF-1 was synthesised from the organic building block shown in Fig. 4.2a. Each building block is surrounded by four more building blocks through eight strong H-bonds involving the

2,4-diaminotriazine groups. The structure exhibits 1D pores running along the *c* axis. One NH₂ group in each ligand is not involved in the H-bonding and is therefore exposed on the pore surface and available to interact with adsorbed species. The C₂H₂ adsorption occurs *via* a 2-step process and displays a large hysteresis, indicating the presence of molecular gates. This step is not seen in the C₂H₄ adsorption isotherm and the uptake is much lower, 8.3 cc g⁻¹ for C₂H₄ vs. 63.2 cc g⁻¹ for C₂H₂ at 273 K and 1 bar (Fig. 4.2). This organic framework shows a C₂H₂/C₂H₄ selectivity of 19.3 at 273 K, much higher than that reported for MOF materials. This is reflected by the large heat of adsorption for C₂H₂ in HOF-1, 58.1 kJ mol⁻¹ which is also higher than most heats of adsorption for C₂H₂ in MOFs. The high C₂H₂ selectivity is achieved through collaborative size-exclusion effect and preferential stronger interactions between the framework and C₂H₂.

a)



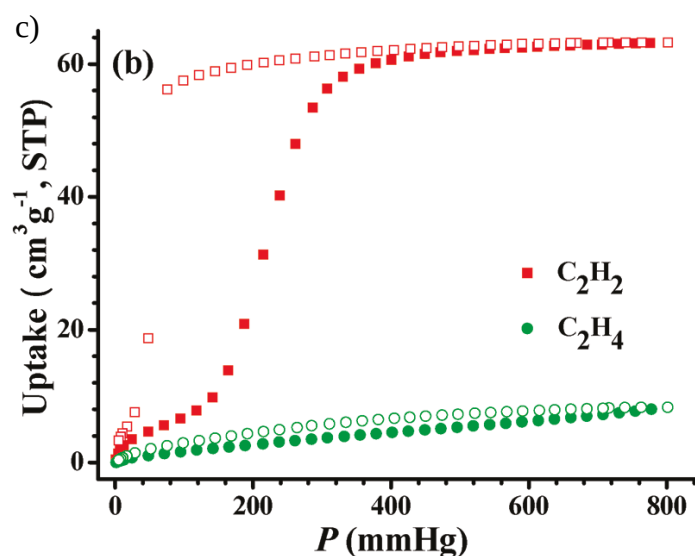
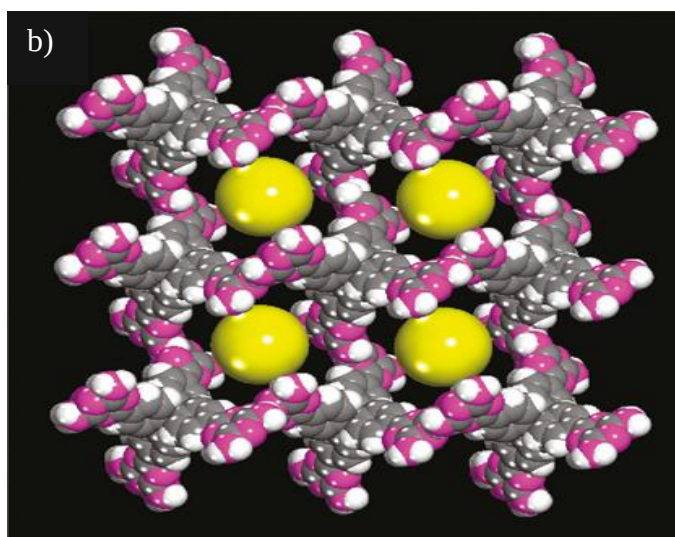


Fig. 4.2 **a)** Organic building block used to construct HOF-1, **b)** View of the crystal structure for HOF-1 showing the pore channels along the *c* axis (available space is filled with yellow balls), **c)** C₂H₂ and C₂H₄ adsorption in HOF-1 at 273 K. Figures taken from reference 10.

The potential for C₂/C₁ hydrocarbon separations has been widely reported and the selectivity is much higher as all C₂ hydrocarbons have the potential to form stronger interactions than CH₄, *i.e.* H-bonds, π - π stacking, dipole interactions *etc.*^{6,11,12} Although CH₄ is smaller which means theoretically more CH₄ can fit inside a pore/channel, the surface area for interaction is smaller.¹³ The reported C₂H₂/CH₄ selectivity for Fe-MOF-74 is ~700 at 318 K and 1 bar and is a direct

result of the large difference in strength of interaction with the framework, reflected by the large difference in heat of adsorption (47 vs. 20 kJ mol⁻¹).¹⁴

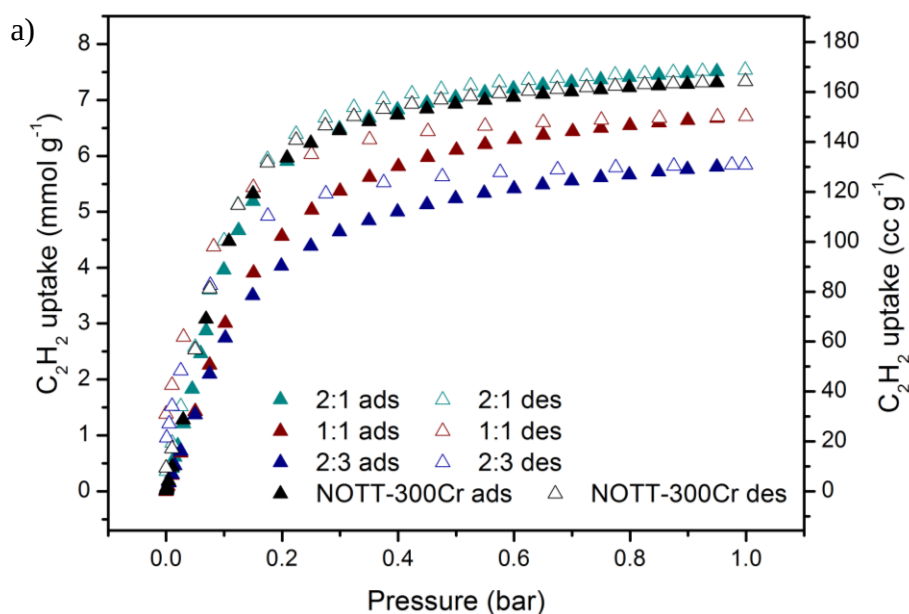
Both open metal sites and size selective adsorption have limitations: open metal sites are unstable in the presence of water vapour and size selective adsorption often has a lower adsorption capacity.^{15,16} The NOTT-300 series contains no open metal centres and instead binds to some adsorbates through weaker H-bonds with the bridging –OH group. The NOTT-300 series has been shown to selectively adsorb CO₂ over other gases (ie N₂, CH₄, CO *etc.*) because of the differences in strength in the H-bonds between the framework and the adsorbed gas. Therefore it is possible that NOTT-300 could selectively adsorb C₂ hydrocarbons through differences in the interaction with the bridging –OH group and possible further interactions with the aromatic phenyl rings in the ligand. In this chapter the adsorption and selectivity of the C₂ hydrocarbons in NOTT-300(Cr) and the NOTT-300(AlCr) series is investigated and the possibility for C₂ hydrocarbon separation is explored. The effect of the cation content present on the adsorption and selectivity is also investigated as it was shown to have an effect in Chapter 3. The adsorption of C₂ hydrocarbons in NOTT-300(Al) is further probed with *in situ* gas loaded INS and PXRD studies. The C₂ selectivity in NOTT-300(Al) is further investigated with dual-component adsorption isotherms and breakthrough experiments.

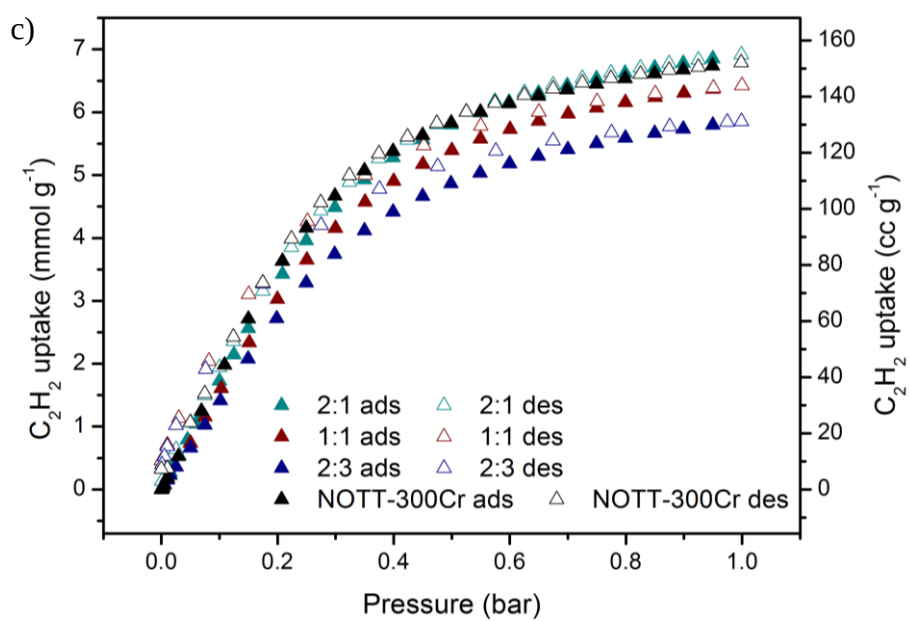
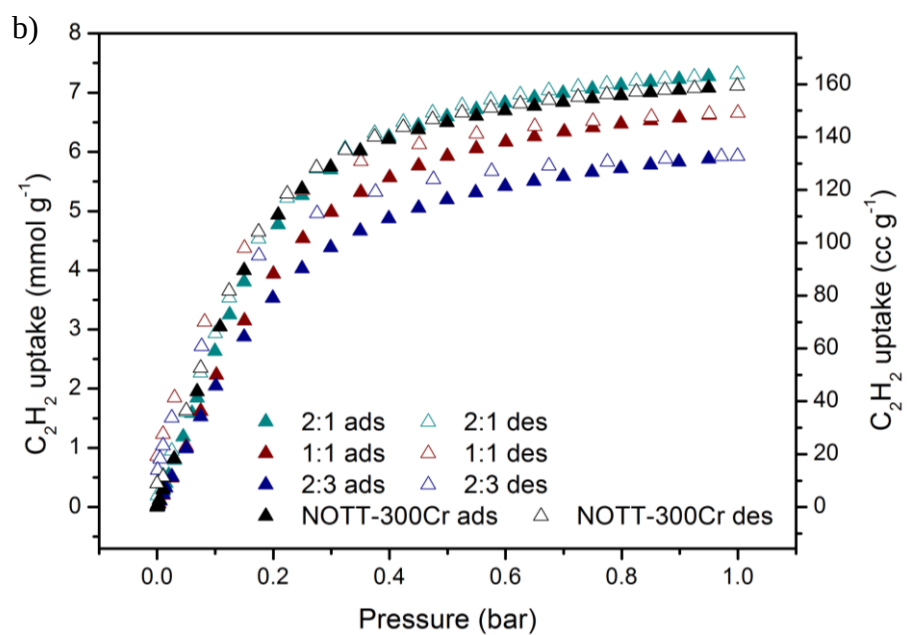
4.2 Results and Discussion

4.2.1 C₂H₂ adsorption in NOTT-300Cr and NOTT-300(AlCr) series

Adsorption isotherms were recorded for all C₂ hydrocarbons in the temperature range of 273 – 303 K and at 0 – 1 bar to investigate the adsorption behaviours of these gases in NOTT-300(Cr) and the NOTT-300(AlCr) series and to assess potential selectivity.

All C₂H₂ adsorption isotherms display a type-I shape with rapid uptake occurring at low pressures before a plateau is reached. This type of shape is indicative of favourable interactions between the framework and the C₂H₂ molecules as these are the dominating factors affecting adsorption at low pressures. Both NOTT-300(Cr) and AlCr2:1 show fully reversible adsorption, with no hysteresis observed upon desorption. However, AlCr1:1 and AlCr2:3 both display a degree of hysteresis upon desorption at all temperatures (Fig. 4.3), although the size of hysteresis does decrease with an increase in temperature so it is possible this is caused by the kinetics of the gas within the sample.





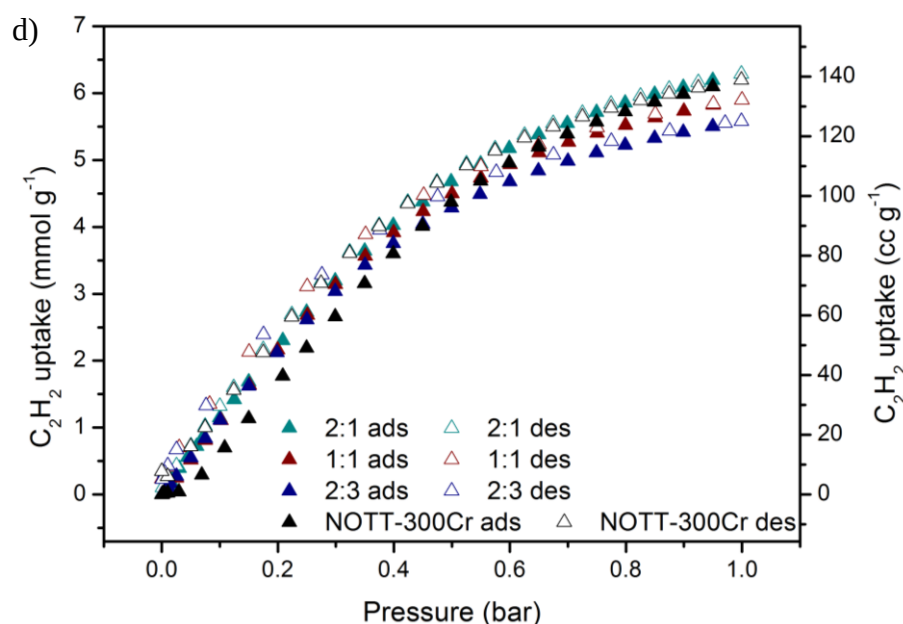


Fig. 4.3 C_2H_2 adsorption isotherms for NOTT-300(Cr), AlCr2:1, AlCr1:1 and AlCr2:3 from 0 to 1 bar at **a)** 273 K, **b)** 283 K, **c)** 293 K, **d)** 303 K.

A summary of C_2H_2 uptake is given in Table 4.1. NOTT-300(AlCr2:1) displays the highest C_2H_2 adsorption capacity at all temperatures recorded, reaching a total uptake of 7.53 mmol g^{-1} at 273 K and 1 bar (Fig. 4.3). NOTT-300(Cr) shows very similar uptakes to AlCr2:1 at all temperatures recorded, with differences of only 0.2 mmol g^{-1} at 273 K and 1 bar. Both AlCr1:1 and AlCr2:3 exhibit much lower uptakes only reaching 6.71 and 5.84 mmol g^{-1} at 273 K and 1 bar, respectively. The C_2H_2 uptake in NOTT-300(Al) under these same conditions is 6.88 mmol g^{-1} . As the C_2H_2 adsorption is high in NOTT-300(Cr), it would be expected for the mixed metal samples with high Cr content to display highest C_2H_2 uptake, however, this is not what was observed. As seen with the CO_2 adsorption, there is clearly more to this than metal content. Both AlCr1:1 and AlCr2:3 show lower adsorption than both single metal MOFs. This behaviour was not observed in CO_2/CH_4 adsorption as all mixed metal samples possessed adsorption capacities somewhere between NOTT-300(Al) and NOTT-300(Cr).

All samples display a decrease in adsorption on increase of temperature except for AlCr2:3 which shows an increase in adsorption (5.84 – 5.93 mmol g⁻¹) when the temperature is increased from 273 – 283 K. It is not known why this occurs as a decrease in adsorption is usually observed when temperature increases. In fact C₂H₂ adsorption in AlCr2:3 appears to vary less as a function of temperature, only reducing by 4.4% from 273 – 303 K. NOTT-300(Cr), AlCr2:1 and AlCr1:1 all show a much greater reduction in uptake when temperature is increased, 15.4% (NOTT-300(Cr)), 16.5% (AlCr2:1) and 12.1% (AlCr1:1).

C ₂ H ₂	AlCr2:1 (mmol g ⁻¹)	AlCr1:1 (mmol g ⁻¹)	AlCr2:3 (mmol g ⁻¹)	NOTT-300(Cr) (mmol g ⁻¹)
273K	7.53	6.71	5.84	7.33
283K	7.31	6.66	5.93	7.12
293K	6.91	6.42	5.85	6.79
303K	6.29	5.90	5.58	6.20

Table 4.1 C₂H₂ uptake in AlCr2:1, AlCr1:1, AlCr2:3 and NOTT-300(Cr) at 1 bar.

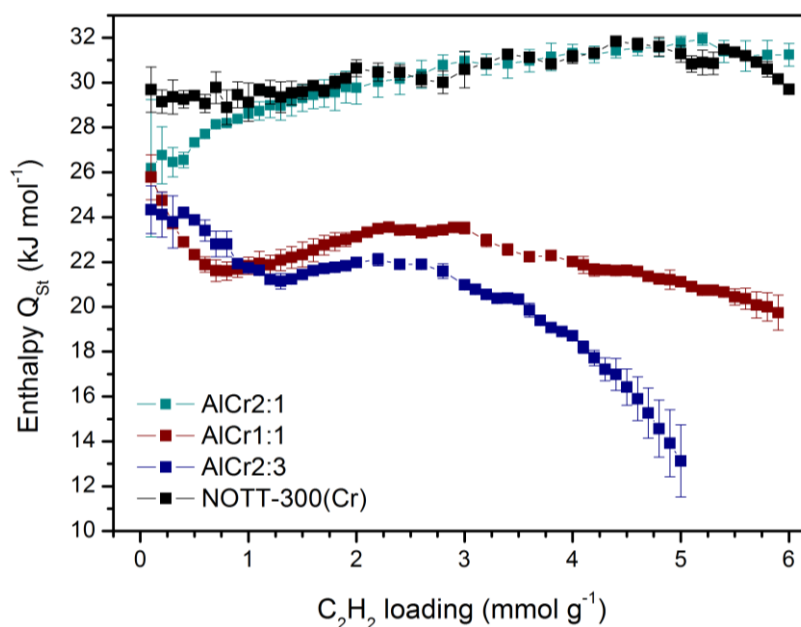
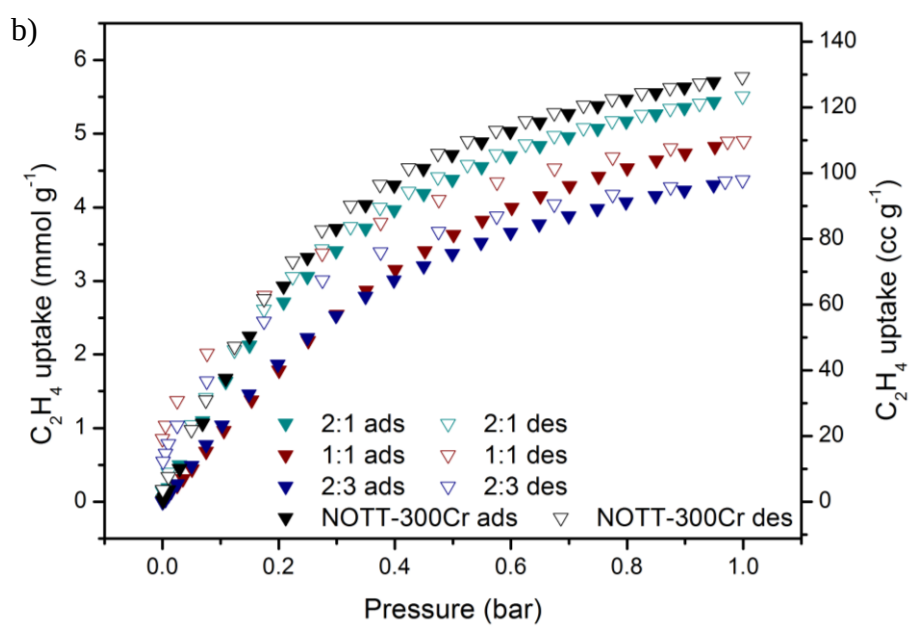
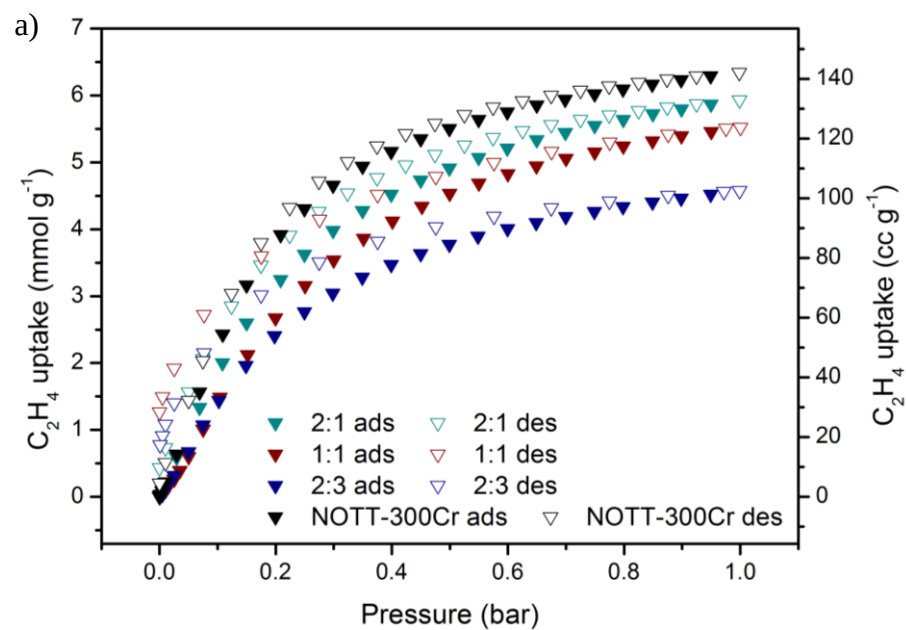


Fig. 4.4 The calculated heats of adsorption for C₂H₂ in NOTT-300(Cr), AlCr2:1, AlCr1:1 and AlCr2:3.

The high heat of adsorption at low loading is indicative of favourable interactions between the framework and the C₂H₂ molecules in all materials. NOTT-300(Cr) displays the highest heat of adsorption at initial C₂H₂ loading (29 kJ mol⁻¹), which increases slightly with further C₂H₂ loading and reaches a total of 31 kJ mol⁻¹ at saturation. The mixed metal materials all show similar heats of adsorption (26 kJ mol⁻¹ for AlCr₂:1, 26 kJ mol⁻¹ for AlCr₁:1 and 24 kJ mol⁻¹ for AlCr₂:3) at initial C₂H₂ loading. With further C₂H₂ loading the heat of adsorption for AlCr₂:1 increases to similar values to NOTT-300(Cr) and also reaches a maximum heat of adsorption of 31 kJ mol⁻¹. The heats of adsorption for AlCr₁:1 and AlCr₂:3 decrease as the amount of adsorbed C₂H₂ increases which may be why the overall uptake for these materials is lower than for NOTT-300(Cr) and AlCr₂:1. Although, why further adsorption would be unfavourable for some materials and not others is not fully known, especially as it can be clearly seen at low loading the C₂H₂ forms favourable interactions with all the framework materials. At higher loadings the interactions between the adsorbed gas becomes the dominating factor facilitating further adsorption so it may be possible there is something preventing these interactions in AlCr₁:1 and AlCr₂:3. If this had been observed in only one sample it is possible the behaviour would not be real and may not be observed again if the measurements are retaken and the heat of adsorption recalculated. However, as this is seen in more than one sample this indicates there must be a cause behind this. The reasons for this are not yet known but could possibly be further probed with C₂H₂-loaded IR studies.

4.2.2 C₂H₄ Adsorption in NOTT-300(Cr) and NOTT-300(AlCr) Series

As with the C₂H₂ adsorption isotherms, the C₂H₄ isotherms all display the same type-I shape. At all temperatures recorded NOTT-300(Cr) possesses the highest C₂H₄ adsorption capacity, reaching a total of 6.34 mmol g⁻¹ at 273 K and 1 bar. NOTT-300AlCr₂:1 displays higher C₂H₄ adsorption than the other mixed metal materials, with an uptake of 5.93 mmol g⁻¹ at 273 K and 1 bar compared to 5.52 mmol g⁻¹ and 4.57 mmol g⁻¹ for AlCr₁:1 and AlCr₂:3 respectively. Under these same conditions (273 K and 1 bar) NOTT-300(Al) reaches a total C₂H₄ uptake of 5.31 mmol g⁻¹. As with C₂H₂ adsorption this value is higher than that obtained for AlCr₂:3 which displays the lowest adsorption capacity at all temperatures. Unlike the case of C₂H₂ there is no increased adsorption with increase in temperature for AlCr₂:3. Among the mixed metal materials there appears to be a trend in C₂H₄ adsorption capacity of AlCr₂:1 > AlCr₁:1 > AlCr₂:3, which leads to a conclusion that higher Cr content leads to lower adsorption capacity. However, this cannot be the case as NOTT-300(Cr) displays the highest C₂H₄ adsorption capacity, much higher than NOTT-300(Al).



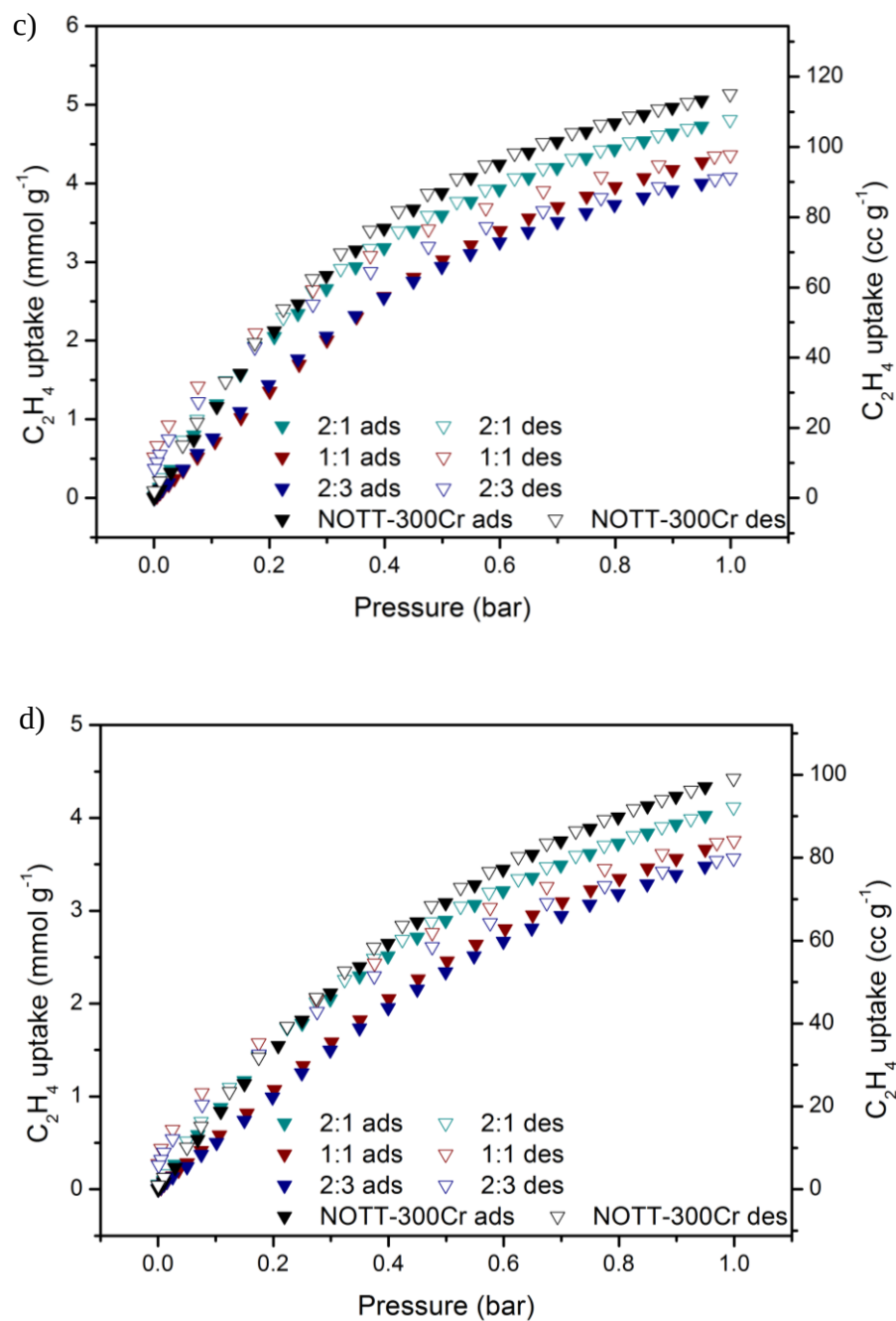


Fig. 4.5 C_2H_4 adsorption isotherms for NOTT-300(Cr), AlCr2:1, AlCr1:1 and AlCr2:3 from 0 to 1 bar at **a)** 273 K, **b)** 283 K, **c)** 293 K and **d)** 303 K.

NOTT-300(Cr) displays fully reversible C_2H_4 adsorption at all temperatures, whereas at 273 K all mixed metal materials display a degree of hysteresis upon desorption. AlCr2:1 shows a much smaller hysteresis than AlCr1:1 and AlCr2:3 and upon increase in temperature the adsorption becomes fully reversible.

However, both AlCr1:1 and AlCr2:3 show hysteresis at all temperatures recorded.

C ₂ H ₄	AlCr2:1 (mmol g ⁻¹)	AlCr1:1 (mmol g ⁻¹)	AlCr2:3 (mmol g ⁻¹)	NOTT-300(Cr) (mmol g ⁻¹)
273K	5.93	5.52	4.57	6.34
283K	5.51	4.91	4.37	5.77
293K	4.81	4.36	4.08	5.14
303K	4.11	3.75	3.57	4.42

Table 4.2 C₂H₄ uptakes in AlCr2:1, AlCr1:1, AlCr2:3 and NOTT-300(Cr) at 1 bar.

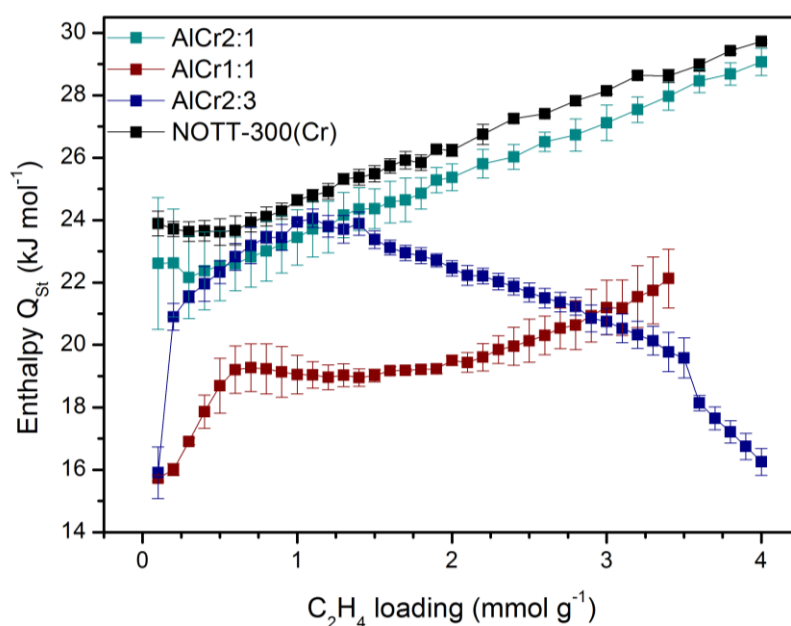


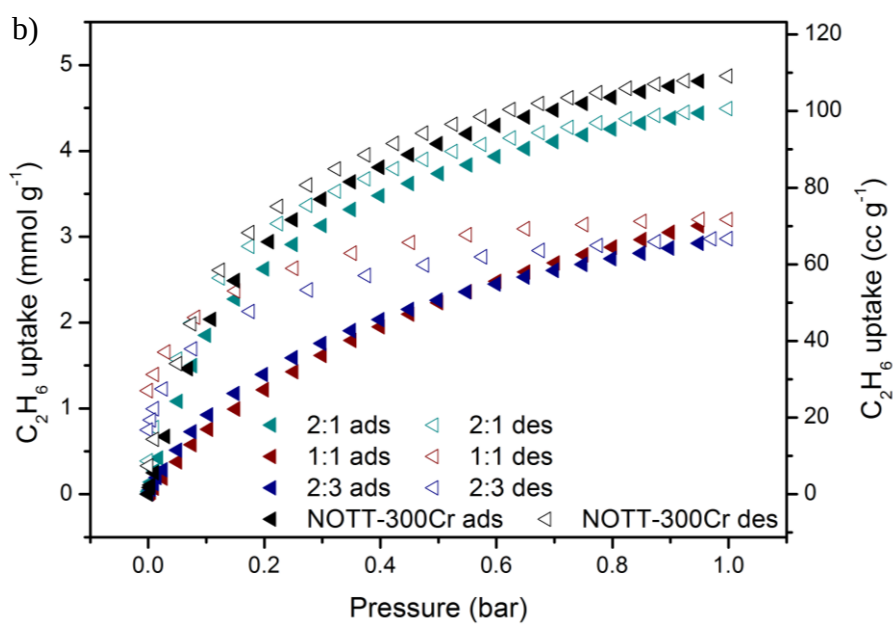
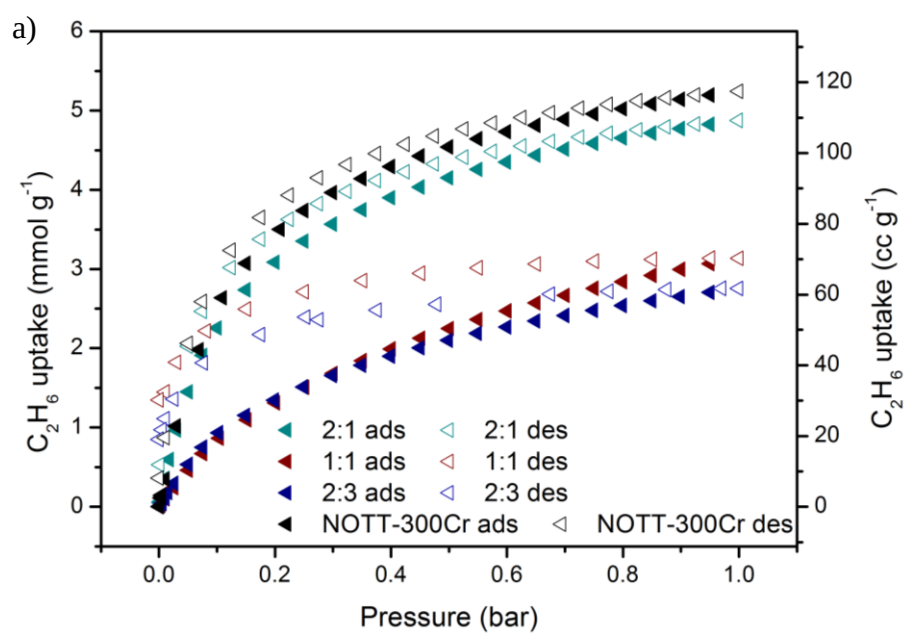
Fig. 4.6 The calculated heats of adsorption for C₂H₄ in NOTT-300(Cr), AlCr2:1, AlCr1:1 and AlCr2:3.

NOTT-300(Cr) and AlCr2:1 both display similar heats of adsorption at initial loading of C₂H₄ of 24 kJ mol⁻¹ and 22 kJ mol⁻¹ respectively and continue to increase with increased loading of C₂H₄. This is indicative of not only favourable interactions between the framework and the adsorbed C₂H₄ molecules, but also strong interactions between the adsorbed C₂H₄ molecules which are observed in liquid C₂H₄.¹⁷ AlCr1:1 also displays this behaviour of increased enthalpy with

increasing amounts of C_2H_4 , however, remains lower than both NOTT-300(Cr) and AlCr2:1, possibly indicating the interactions in AlCr1:1 are weaker. The curve of the heat of adsorption for AlCr2:3 does not display the same shape, with an initial increase in enthalpy with increase in loading, from 16 to 24 kJ mol⁻¹ at 0.1 to 1.5 mmol g⁻¹. Above 1.5 mmol g⁻¹ the heat of adsorption decreases leading to speculation that these strong C_2H_4 - C_2H_4 interactions are not present in this sample, however, there is no obvious reason as to why that would occur as all materials have the same structure.

4.2.3 C_2H_6 Adsorption in NOTT-300(Cr) and NOTT-300(AlCr) Series

All C_2H_6 adsorption isotherms recorded show the same type-I shape and all display a hysteresis upon desorption. However, there appears to be a clear difference in C_2H_6 adsorption behaviour between NOTT-300(Cr) and AlCr2:1 compared to AlCr1:1 and AlCr2:3. Both NOTT-300(Cr) and AlCr2:1 exhibit higher C_2H_6 adsorption capacities, steeper adsorption at low pressures and a smaller hysteresis on desorption. This steeper adsorption at low pressures indicates that there are beneficial interactions between C_2H_6 and the frameworks, however, since the structures of all materials are the same and only vary on metal content if these interactions are occurring it would be expected for them to occur in all materials. Therefore there must be another driving force behind this adsorption behaviour, perhaps a difference in the diffusion kinetics of the gases within the channel. The large difference in C_2H_6 uptake decreases when the temperature is increased, this is because the uptake in both NOTT-300(Cr) and AlCr2:1 decrease and the uptake in AlCr1:1 and AlCr2:3 actually increase.



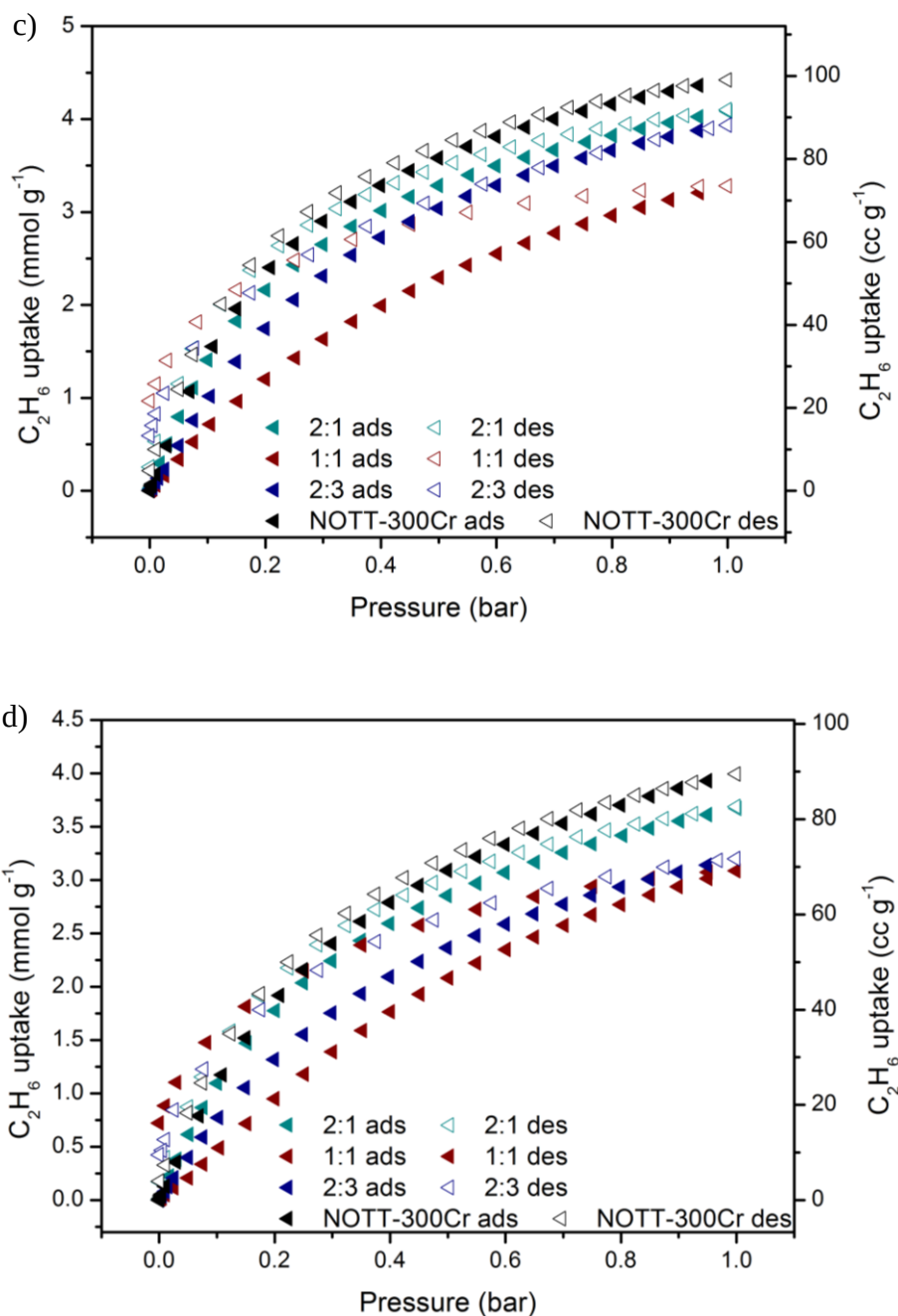


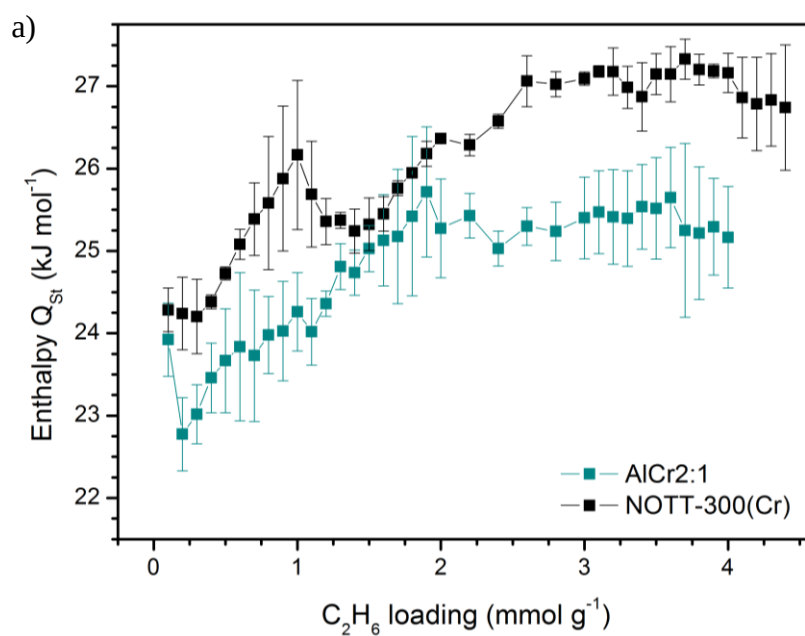
Fig. 4.7 C_2H_6 adsorption isotherms for NOTT-300(Cr), AlCr2:1, AlCr1:1 and AlCr2:3 from 0 to 1 bar at **a)** 273 K, **b)** 283 K, **c)** 293 K and **d)** 303 K.

NOTT-300(Cr) shows the highest adsorption capacity for C_2H_6 at all temperatures recorded, reaching a total uptake of 5.24 mmol g^{-1} at 273 K and 1 bar. The C_2H_6 adsorption in both AlCr1:1 and AlCr2:3 appears to initially increase with an increase in temperature from 273 – 293 K. At 273 K and 283 K AlCr2:3 displays the lowest C_2H_6 adsorption, as it has with all other C_2

hydrocarbons. However at 293 K and 303 K the uptakes for AlCr2:3 surpass those recorded for AlCr1:1, making AlCr1:1 the lowest C₂H₆ adsorbing material under these conditions.

C ₂ H ₆	AlCr2:1 (mmol g ⁻¹)	AlCr1:1 (mmol g ⁻¹)	AlCr2:3 (mmol g ⁻¹)	NOTT-300(Cr) (mmol g ⁻¹)
273 K	4.88	3.14	2.75	5.24
283 K	4.49	3.20	2.98	4.87
293 K	4.08	3.28	3.94	4.42
303 K	3.67	3.09	3.20	3.99

Table 4.3 C₂H₆ uptakes in AlCr2:1, AlCr1:1, AlCr2:3 and NOTT-300(Cr) at 1 bar.



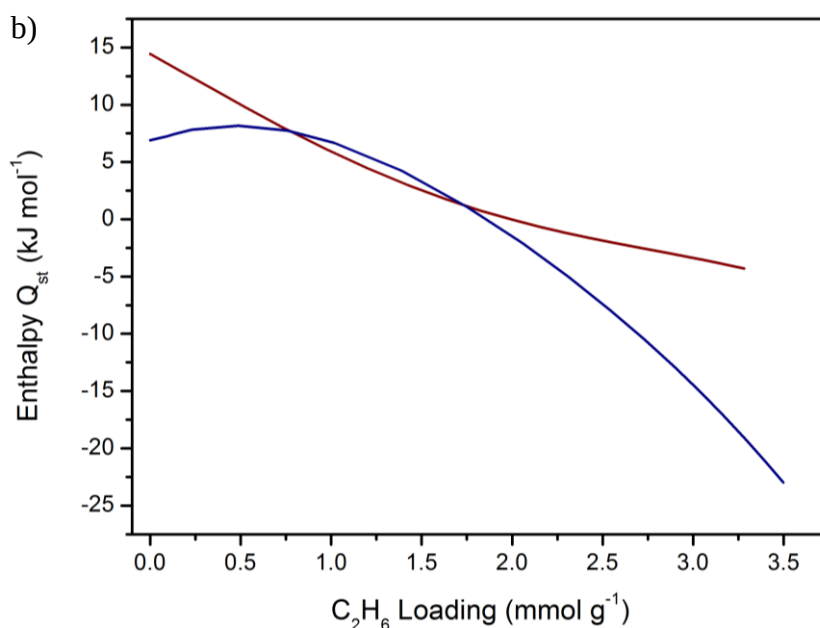


Fig. 4.8 The calculated heats of adsorption for C₂H₆ in **a)** NOTT-300(Cr) and AlCr2:1 and **b)** AlCr1:1 (red) and AlCr2:3 (blue).

Owing to the increased C₂H₆ adsorption with increase in temperature for both AlCr1:1 and AlCr2:3 the van't Hoff isochore was not used and instead the heat of adsorption for C₂H₆ in these two materials was calculated using the virial equation (Equation 4.1).

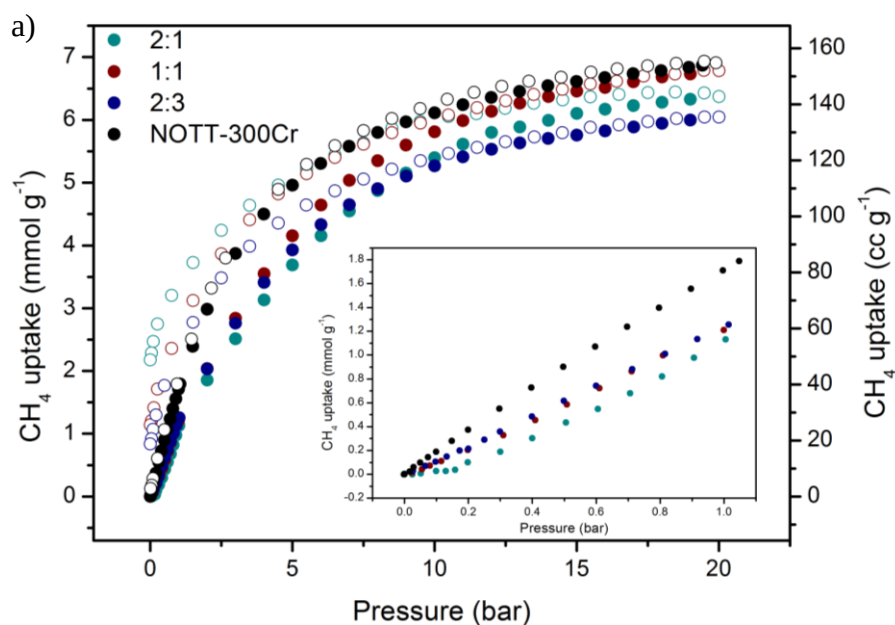
$$\ln(n/p) = A_0 + A_1 n^1 + A_2 n^2 \dots \dots (4.1)$$

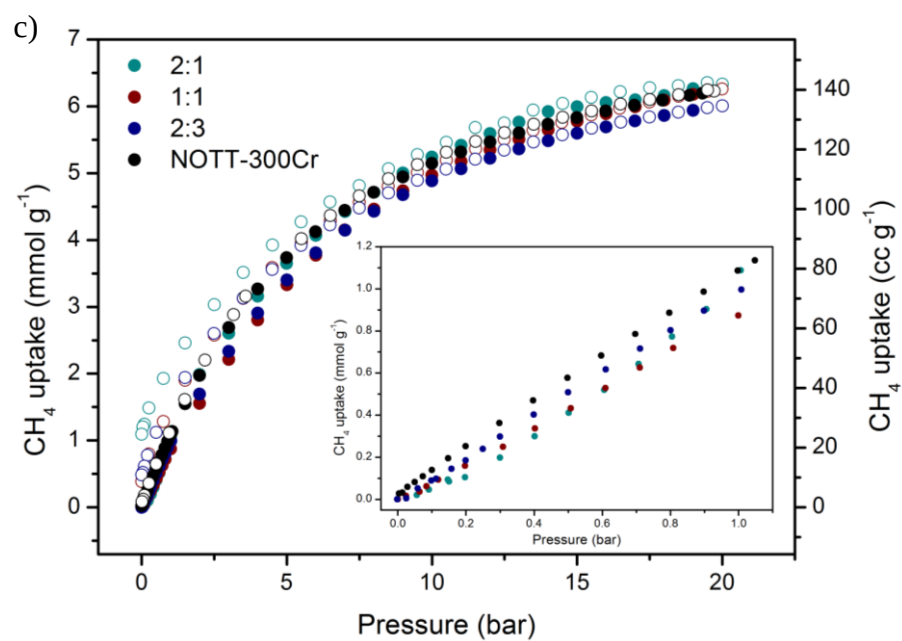
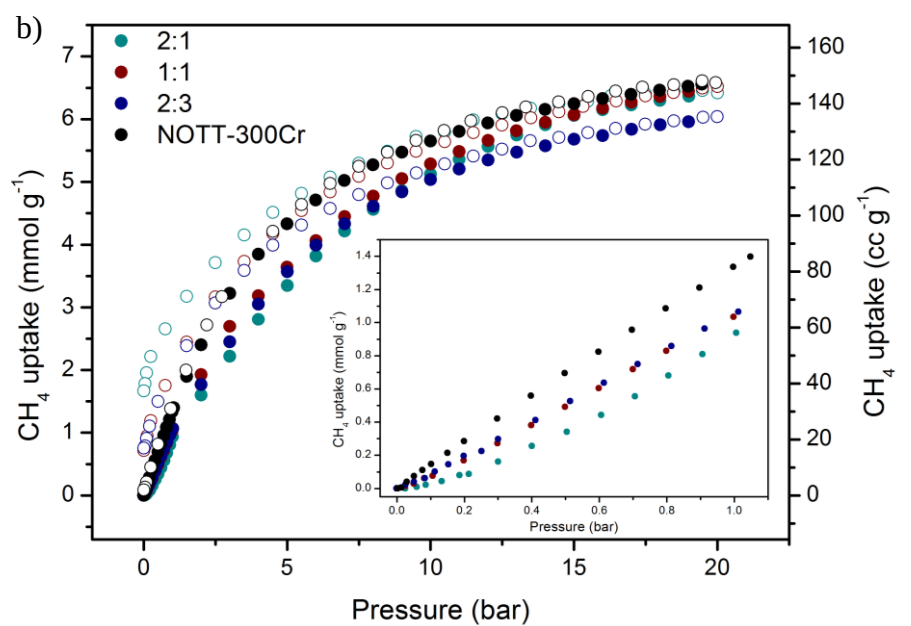
The calculated heat of adsorption for both NOTT-300(Cr) and AlCr2:1 is ~24 kJ mol⁻¹ at initial C₂H₆ loading for both materials. The enthalpy increases for both materials with increased amounts of C₂H₆ reaching 25 and 27 kJ mol⁻¹ for AlCr2:1 and NOTT-300(Cr) respectively. Both AlCr1:1 and AlCr2:3 display lower heats of adsorption at initial C₂H₆ loading, ~15 kJ mol⁻¹ and ~8 kJ mol⁻¹ respectively. However, both materials also display lower C₂H₆ uptakes when compared with NOTT-300(Cr) and AlCr2:1, so a lower heat of adsorption is to be expected. The moderate heat of adsorption displayed by NOTT-300(Cr) and

AlCr₂:1 could indicate favourable interactions between the C₂H₆ molecules and the framework; this could be due to the polarizability of C₂H₆, as there is no π electron system to interact with the –OH group.

4.2.4 CH₄ Adsorption in NOTT-300(Cr) and NOTT-300(AlCr) Series

CH₄ adsorption isotherms were also recorded, as CH₄ separation from C₂ hydrocarbons is an industrially relevant process. CH₄ adsorption isotherms were recorded at 273 – 303 K and 0 – 20 bar. As has been previously shown with C₂ hydrocarbon adsorption, the CH₄ adsorption behaviour varies greatly across the NOTT-300 series with respect to temperature and pressure with no discernible trend.





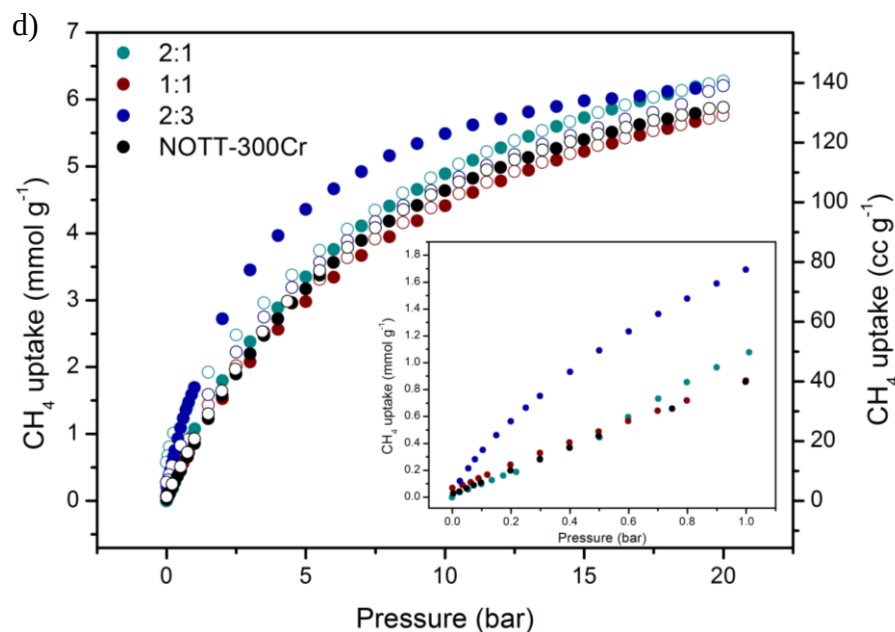


Fig. 4.9 CH₄ adsorption isotherms for NOTT-300(Cr), AlCr₂:1, AlCr₁:1 and AlCr₂:3 from 0 to 1 bar at **a)** 273 K, **b)** 283 K, **c)** 293 K and **d)** 303 K.

The CH₄ adsorption behaviour displayed by the NOTT-300 series is different to that observed for the C₂ hydrocarbon adsorption, for example, there is no one sample that displays the highest uptake capacity at all temperatures. At 273 K and 283 K NOTT-300(Cr) shows the highest CH₄ uptakes, reaching 6.91 and 6.58 mmol g⁻¹ respectively at 20 bar. However upon further increase in temperature, at 293 K and 303 K it is AlCr₂:1 that shows the highest CH₄ adsorption at 20 bar, with uptakes of 6.33 and 6.27 mmol g⁻¹, respectively. Both NOTT-300(Cr) and AlCr₁:1 show a decrease in uptake with increase in temperature; however, that is not the case for AlCr₂:1 and AlCr₂:3. AlCr₂:1 displays an initial increase in CH₄ adsorption capacity when temperature is increased from 273 – 283 K, but upon further increase in temperature the total CH₄ uptake reduces. The CH₄ adsorption in AlCr₂:3 does not appear to change when temperature is increased from 273 – 283 K remaining at 6.04 mmol g⁻¹ and

only slightly reduces at 293 K to 6.01 mmol g⁻¹. The CH₄ uptake capacity is then increased at 303 K, giving the highest CH₄ uptake shown by AlCr₂:3.

The 1 bar values are also of importance for comparison with the uptakes of C₂ hydrocarbons and selectivity calculations. The adsorption behaviour displayed at 1 bar is similar to that displayed at 20 bar, for instance NOTT-300(Cr) displays the highest uptakes at 273 K and 283 K at 1 bar. At 303 K and 1 bar NOTT-300(AlCr₂:3) displays the highest CH₄ uptake.

CH ₄	AlCr ₂ :1 (mmol g ⁻¹)	AlCr ₁ :1 (mmol g ⁻¹)	AlCr ₂ :3 (mmol g ⁻¹)	NOTT-300(Cr) (mmol g ⁻¹)
273 K	6.37 (1.13)	6.78 (1.21)	6.04 (1.25)	6.91 (1.79)
283 K	6.42 (0.94)	6.52 (1.03)	6.04 (1.06)	6.58 (1.34)
293 K	6.33 (1.09)	6.26 (0.87)	6.01 (0.99)	6.23 (1.09)
303 K	6.27 (1.07)	5.76 (0.86)	6.21 (1.69)	5.88 (0.85)

Table 4.4 CH₄ uptake in AlCr₂:1, AlCr₁:1, AlCr₂:3 and NOTT-300(Cr) at 20 bar, values in ()

denote 1 bar uptake.

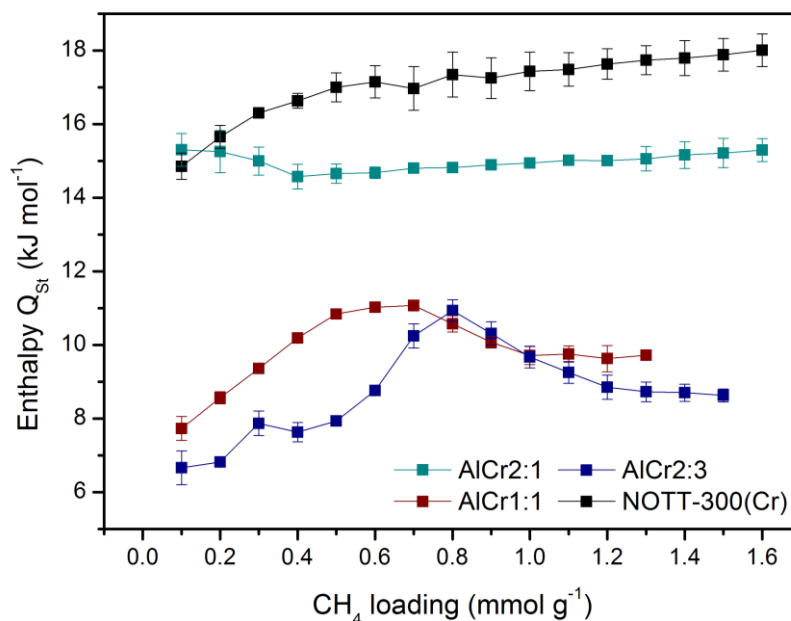


Fig. 4.10 The calculated heats of adsorption for CH₄ in NOTT-300(Cr), AlCr2:1, AlCr1:1 and AlCr2:3.

AlCr2:1 shows a heat of adsorption at initial CH₄ loading of ~15 kJ mol⁻¹, which does not appear to change much across the entire CH₄ loading range (14.5 – 15.5 kJ mol⁻¹). The heat of adsorption for NOTT-300(Cr) is very similar to AlCr2:1 at low loadings of CH₄, ~15 kJ mol⁻¹, however unlike AlCr2:1 this increases gradually with further CH₄ loading to a total of 18 kJ mol⁻¹. The calculated heats of adsorption for AlCr1:1 and 2:3 show similar shapes; a low heat of adsorption at initial CH₄ loading (AlCr1:1 – 7 kJ mol⁻¹, AlCr2:3 – 6 kJ mol⁻¹) and reach a maximum enthalpy at ~ 0.7 mmol g⁻¹, ~ 11 kJ mol⁻¹ for both AlCr1:1 and AlCr2:3. The heats of adsorption for CH₄ are much lower than those calculated for the C₂ hydrocarbons as CH₄ is unable to form any of these favourable interactions that are formed by C₂H₂ (π electron system), C₂H₄ (π electron system) and C₂H₆ (high polarizability).

4.2.5.1 Calculated C₂-Hydrocarbon Selectivities for NOTT-300(Cr) and AlCr Series

The C₂ hydrocarbon and CH₄ adsorption in NOTT-300(Cr) and the NOTT-300(AlCr) series vary greatly with respect to sample and temperature. This means that the selectivity will vary across the MOF series. Low energy separation of mixtures found in the same fraction is of great industrial importance. Ethylene is a feedstock for many organic industrial processes, especially in the production of plastics and acetylene has applications in welding and metal work. Ethane is used as a precursor for ethylene production and is also used as a refrigerant in very low refrigeration systems.

High C₂H₂/C₂H₄ selectivity is difficult to achieve in MOFs owing to their similar sizes and properties. Both species have the ability to interact with open metal sites so selectivity is often achieved by molecular sieving type effects, however, this often causes the total uptake capacity to be low. NOTT-300(Cr) shows the lowest C₂H₂/C₂H₄ selectivity, only reaching a maximum of 2 at 273 K and 1 bar. At 303 K there is no selectivity displayed by NOTT-300(Cr). The highest calculated C₂H₂/C₂H₄ selectivity is 3 and this selectivity is displayed by all the mixed metal materials at different temperatures: AlCr₂:1 – 273 K, AlCr₁:1 - 283 and 293 K, AlCr₂:3 – 273 and 283 K. The calculated C₂H₂/C₂H₄ selectivity, although low, is higher than some literature examples such as Fe₂(dobdc) which only has a selectivity of 1.8 as calculated by IAST.¹⁸ M¹MOF-3a shows a higher selectivity (~5), however, as previously mentioned, the size selective process through which this material achieves the selectivity leads to a lower total adsorption capacity.¹⁹

C ₂ H ₂ / C ₂ H ₄	AlCr2:1		AlCr1:1		AlCr2:3		NOTT-300(Cr)	
	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST
273 K	2.3	2.9	1.9	2.4	1.9	2.6	1.9	2.4
283 K	1.8	2.3	2.3	2.7	2.0	2.5	1.8	2.2
293 K	1.6	2.1	2.3	2.5	1.8	2.2	1.7	2.0
303 K	1.5	1.8	2.0	2.2	2.2	2.4	1.2	1.3

Table 4.5 Calculated C₂H₂/C₂H₄ selectivity for AlCr2:1, AlCr1:1, AlCr2:3 and NOTT-300(Cr)

at 1 bar.

The C₂H₂/C₂H₆ selectivity is much greater throughout the series, but is still quite low for NOTT-300(Cr) and AlCr2:1 which only reach a maximum selectivity of 3.2. AlCr1:1 and AlCr2:3 show much greater C₂H₂/C₂H₆ selectivity, as high as 7.8 for both materials at 273 K and 1 bar. At 293 - 303 K and 1 bar AlCr1:1 displays the highest selectivity. The C₂H₆ adsorption in AlCr2:3 increases at these temperatures, whereas the C₂H₂ adsorption decreases, leading to a lower selectivity. There are many examples in the literature of higher C₂H₂/C₂H₆ selectivity such as, Fe₂(dobdc),¹⁸ Mg₂(dobdc)⁵ and Cu-BTC,²⁰ these frameworks all contain unsaturated metal centres after activation which are available to bind with C₂H₂ molecules more favourably than C₂H₆. However, these MOFs are often unstable to the presence of water making them unusable in many industrial processes.

C ₂ H ₂ / C ₂ H ₆	AlCr2:1		AlCr1:1		AlCr2:3		NOTT-300(Cr)	
	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST
273 K	1.7	3.2	3.1	7.8	2.6	7.8	1.4	2.8
283 K	1.3	2.6	2.8	5.5	2.1	4.6	1.4	2.3
293 K	1.6	2.1	2.2	3.7	1.4	2.0	1.2	2.9
303 K	1.0	1.7	2.3	2.9	1.4	2.2	0.8	1.1

Table 4.6 Calculated C₂H₂/C₂H₆ selectivity for AlCr2:1, AlCr1:1, AlCr2:3 and NOTT-300(Cr)

at 1 bar.

The C_2H_4/C_2H_6 selectivity shown by NOTT-300(Cr) and AlCr2:1 is almost non-existent; in fact both materials show a slight favour towards C_2H_6 adsorption. However, when calculated the C_2H_6/C_2H_4 selectivity is also low/negligible, the highest reaching only 1.4 (ratio of isotherm slopes). Both AlCr1:1 and AlCr2:3 display higher C_2H_4/C_2H_6 selectivity, particularly at lower temperatures, 2.7 for AlCr1:1 and 2.5 for AlCr2:3 at 273 K and 1 bar. At higher temperatures (293 K) the C_2H_4/C_2H_6 selectivity for AlCr1:1 and AlCr2:3 is reduced to ~ 1 , indicating there is no preferential adsorption of C_2H_4 over C_2H_6 in either AlCr1:1 or AlCr2:3. This is because both C_2H_4 and C_2H_6 lack a dipole moment and are equally polarisable and so will form similar strength H-bonds/interactions with the framework.

C_2H_4/C_2H_6	AlCr2:1		AlCr1:1		AlCr2:3		NOTT-300(Cr)	
	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST
273 K	0.7	0.9	1.6	2.7	1.3	2.5	0.8	1.1
283 K	0.8	1.0	1.2	1.8	1.0	1.6	0.8	1.0
293 K	0.7	0.9	0.9	1.3	0.7	0.9	0.7	0.9
303 K	0.7	0.9	1.1	1.2	0.6	0.8	0.7	0.8

Table 4.7 Calculated C_2H_4/C_2H_6 selectivity for AlCr2:1, AlCr1:1, AlCr2:3 and NOTT-300(Cr)

at 1 bar.

C_2H_6/C_2H_4	AlCr2:1		AlCr1:1		AlCr2:3		NOTT-300(Cr)	
	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST
273 K	1.4	1.0	0.6	0.4	0.7	0.4	1.3	0.9
283 K	1.3	1.0	0.8	0.6	0.9	0.6	1.3	1.0
293 K	1.4	1.1	1.0	0.8	1.4	1.2	1.4	1.1
303 K	1.4	1.2	0.8	0.8	1.6	1.2	1.4	1.2

Table 4.8 Calculated C_2H_6/C_2H_4 selectivity for AlCr2:1, AlCr1:1, AlCr2:3 and NOTT-300(Cr)

at 1 bar.

The separation of C_2/C_1 hydrocarbons is of industrial importance for many applications: the purification of natural gas and the purification of C_2 hydrocarbons for chemical feedstock are just two examples. The separation of C_2/C_1 hydrocarbons is easier to achieve in MOFs than the separations of the C_2 hydrocarbons, owing to their different sizes, polarizability and quadrupole moments.

The C_2H_2/CH_4 selectivity calculated for the NOTT-300 series (Table 4.9) is reasonably high, owing to the large differences in interaction between C_2H_2 and CH_4 with the framework. AlCr2:1 displays the highest C_2H_2/CH_4 selectivity at all temperatures recorded, except for 303 K where AlCr1:1 shows a slightly higher selectivity. AlCr2:3 displays a large reduction in selectivity at 303 K, this is likely due to the increased CH_4 adsorption observed at 303 K. There are many reported selectivities greater than those calculated for the NOTT-300 series, *i.e.* $Fe_2(dobdc)$ which has a calculated C_2H_2/CH_4 selectivity greater than 700 at 318 K. This high selectivity is because of the difference in heat of adsorption for the adsorbed gases arising from the strong interaction between C_2H_2 with the open Fe sites, whereas CH_4 forms no such interaction with the open metal sites.

The C_2H_4/CH_4 selectivity is overall much lower than C_2H_2/CH_4 selectivity because C_2H_4 forms weaker interactions with the framework compared to C_2H_2 . AlCr2:1 shows the highest C_2H_4/CH_4 selectivity at all temperatures except for 303 K where AlCr2:1 and NOTT-300(Cr) have similar selectivities (Table 4.10).

The C_2H_6/CH_4 selectivity appears to vary the most across the series as a function of temperature, with AlCr1:1 and AlCr2:3 showing higher selectivities at 293 K than at 273 K (AlCr1:1 - 7.3 vs. 6.1, AlCr 2:3 – 9.7 vs. 6.2) (Table 4.11).

However, even with the increase in selectivity NOTT-300(Cr) and AlCr2:1 show higher C₂H₆/CH₄ selectivity than AlCr1:1 and AlCr2:3 at all temperatures. The highest C₂H₆/CH₄ selectivity for the series is 22.7, calculated for AlCr2:1 at 273 K and 1 bar.

C ₂ H ₂ /CH ₄	AlCr2:1		AlCr1:1		AlCr2:3		NOTT-300(Cr)	
	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST
273 K	25.5	51.3	26.9	27.2	24.8	24.8	22.2	32.5
283 K	20.8	36.8	23.4	23.8	20.4	22.1	19.2	23.8
293 K	16.3	20.3	18.7	20.2	14.0	16.3	15.7	19.5
303 K	13.4	13.4	12.2	14.4	4.6	6.0	11.4	10.2

Table 4.9 Calculated C₂H₂/CH₄ selectivity for AlCr2:1, AlCr1:1, AlCr2:3 and NOTT-300(Cr)

at 1 bar.

C ₂ H ₄ /CH ₄	AlCr2:1		AlCr1:1		AlCr2:3		NOTT-300(Cr)	
	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST
273 K	11.7	19.6	12.8	12.2	13.0	11.2	11.9	13.6
283 K	11.8	18.2	9.7	9.1	10.1	9.8	10.3	11.5
293 K	10.4	11.0	8.3	8.3	7.5	7.8	9.1	10.0
303 K	9.5	8.0	6.2	6.2	2.1	2.4	8.7	9.1

Table 4.10 Calculated C₂H₄/CH₄ selectivity for AlCr2:1, AlCr1:1, AlCr2:3 and NOTT-300(Cr)

at 1 bar.

C ₂ H ₆ /CH ₄	AlCr2:1		AlCr1:1		AlCr2:3		NOTT-300(Cr)	
	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST	Ratio of isotherm slopes	IAST
273 K	14.7	22.7	7.9	6.1	8.9	6.2	15.4	14.5
283 K	15.0	13.4	8.0	5.2	9.9	7.6	13.2	13.8
293 K	14.1	12.7	8.4	7.3	9.8	9.7	12.6	12.5
303 K	13.4	10.0	5.1	5.2	3.3	3.1	12.7	12.0

Table 4.11 Calculated C₂H₆/CH₄ selectivity for AlCr2:1, AlCr1:1, AlCr2:3 and NOTT-300(Cr)

at 1 bar.

Both selectivity calculations show that all materials in the NOTT-300 series are capable of separating C_2/C_1 hydrocarbon mixtures at 273 – 303 K. The separation of C_2 hydrocarbons however, was more complicated/varied. With almost no selectivity for either gas in a C_2H_4/C_2H_6 mixture, a low selectivity should be expected as both gases give similar heats of adsorption in all NOTT-300 materials. High C_2H_4/C_2H_6 selectivity in the literature is often found in materials with unsaturated metal centres as C_2H_6 will not strongly bind to the open metal centre. NOTT-300 only forms weak/moderate H-bonds and van der Waals interactions with adsorbed gases, much weaker interactions than those between adsorbed gas and unsaturated metal centres. However, the cumulative effects of these weak – moderate interactions still leads to preferential adsorption of the C_2 hydrocarbons over CH_4 . The C_2H_2/C_2H_4 and C_2H_2/C_2H_6 selectivities in these materials were much greater, owing to the stronger interaction between the bridging –OH group and adsorbed C_2H_2 molecules. The material with the highest C_2H_2/C_2H_4 selectivity is dependent on temperature, leading to the possibility of choosing a material for the separation based on the temperature at which it is carried out. At 273 K and 1 bar it is AlCr2:1 that displays the greatest C_2H_2/C_2H_4 selectivity (2.9), whereas at 293 K AlCr1:1 shows a greater selectivity compared with AlCr2:1 (2.5 vs. 2.1).

4.2.5.2 C_2 -Hydrocarbon Selectivity in NOTT-300(Al)

C_2 hydrocarbon adsorption isotherms were carried out for NOTT-300(Al) at 293 K and 0 – 1 bar for comparison with the dual-component adsorption isotherms and this data was used to calculate the selectivity for NOTT-300(Al) at 293 K.

NOTT-300(Al) displays exceptional C_2H_x/CH_4 selectivity at 293 K, much higher than the selectivities calculated for NOTT-300(Cr) and the AlCr series. This is due to the extremely low CH_4 adsorption capacity in NOTT-300(Al). The selectivities for C_2 separations are also much higher in NOTT-300(Al) than those calculated for NOTT-300(Cr) and the AlCr series. This could be due to the restricted space available in NOTT-300(Al); the strong interactions formed between the framework and the C_2H_2 molecules help to overcome this restriction. NOTT-300(Cr) did not display any selectivity for C_2H_4/C_2H_6 gas mixtures owing to similar heats of adsorption, whereas, NOTT-300(Al) shows moderate a C_2H_4/C_2H_6 selectivity of 3.1 at 293 K. This is likely a combination of the difference in strength between C_2H_4 or C_2H_6 and the framework and a difference in the kinetics of the gas diffusion along the channel. C_2H_6 has slower kinetics than C_2H_4 in NOTT-300(Al). This selectivity is not shown in NOTT-300(Cr) because it has a slightly larger pore and so diffusion is not restricted, allowing C_2H_4 and C_2H_6 to travel along the channel at similar rates.

NOTT-300(Al)	Ratio of isotherm slopes	IAST
C_2H_2/C_2H_4	3.4	4.3
C_2H_2/C_2H_6	5.3	28.2
C_2H_4/C_2H_6	1.6	3.1
C_2H_2/CH_4	192.5	132.9
C_2H_4/CH_4	56.9	37.3
C_2H_6/CH_4	36.1	18.8

Table 4.12 Calculated selectivities for NOTT-300(Al) at 1 bar and 293 K.

4.2.6 Dual Component Adsorption Isotherms

4.2.6.1 Dual Component Adsorption Isotherms for NOTT-300(Al)

A series of dual component adsorption isotherms were conducted for NOTT-300(Al) at 293 K using a variety of mixtures to further probe the adsorption and selectivity of C_2 hydrocarbons in this material.

The C_2H_2/C_2H_4 dual component adsorption isotherm reaches a total uptake of 16.8 wt% at 293 K and 1 bar, this is in good agreement with the IAST predicted uptake (16.0 wt%) showing the compatibility of these two techniques. The slightly higher experimental uptake recorded indicates an enhanced selectivity in practical C_2H_2/C_2H_4 separations. The C_2H_2 uptake at 0.5 bar is 15.2 wt%, showing that the majority adsorbed gas is C_2H_2 .

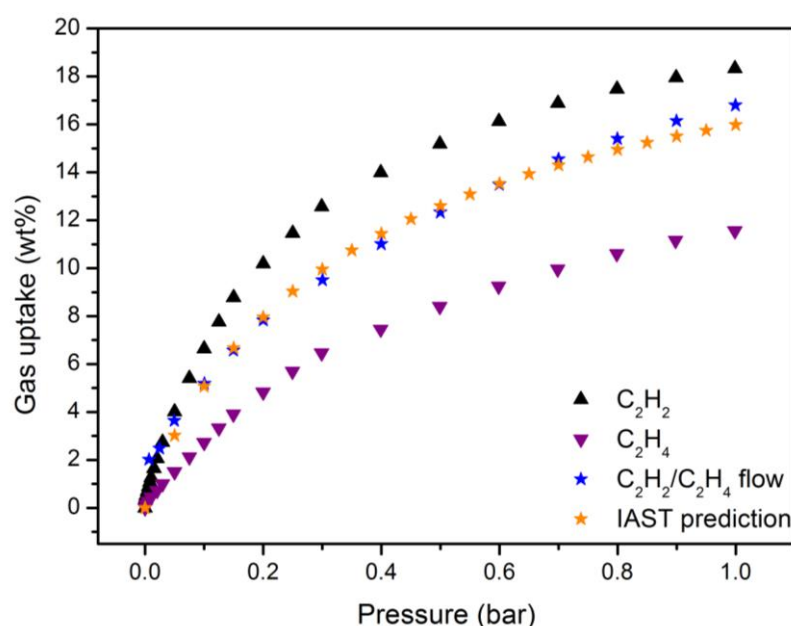


Fig. 4.11 Dual component adsorption isotherm for a 1:1 C_2H_2/C_2H_4 mixture at 293 K from 0 to 1 bar in NOTT-300(Al).

The calculated C_2H_2/C_2H_6 selectivity is higher than that calculated for C_2H_2/C_2H_4 indicating that the separation of C_2H_2/C_2H_6 will be more efficient

than C_2H_2/C_2H_4 . The experimental uptake recorded for C_2H_2/C_2H_6 is 13.4 wt%, which is lower than the IAST predicted uptake of 14.9 wt%. This is potentially owing to the slow kinetics of C_2H_6 , which restricts the adsorption and could also slow down the diffusion of C_2H_2 leading to a lower observed uptake.

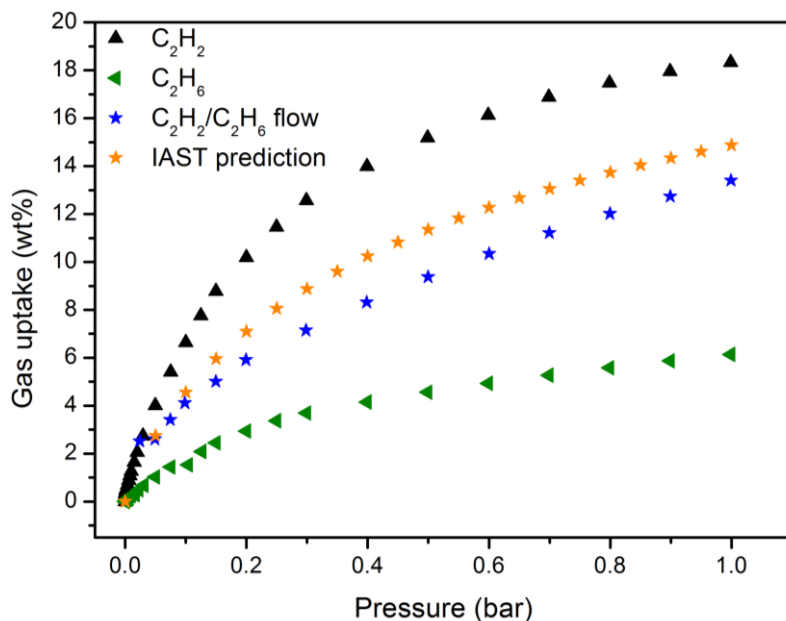


Fig. 4.12 Dual component adsorption isotherm for a 1:1 C_2H_2/C_2H_6 mixture at 293 K from 0 to 1 bar in NOTT-300(Al).

Unlike any of the Cr containing frameworks NOTT-300(Al) displayed reasonable C_2H_4/C_2H_6 selectivity at 293 K. There is a larger difference in uptake between C_2H_4 and C_2H_6 for NOTT-300(Al), which can be clearly seen in Fig. 4.13. The experimental uptake recorded for a 1:1 mix of C_2H_4 and C_2H_6 reaches a total of 9.2 wt% at 293 K and 1 bar, which matches closely with the IAST prediction of 9.0 wt%. The corresponding uptake of pure C_2H_4 at 0.5 bar is 8.4 wt% whereas the C_2H_6 uptake only reaches 4.5 wt% under these same conditions. The dual component adsorption isotherm clearly supports the high selectivity calculated for C_2H_4 over C_2H_6 for NOTT-300(Al).

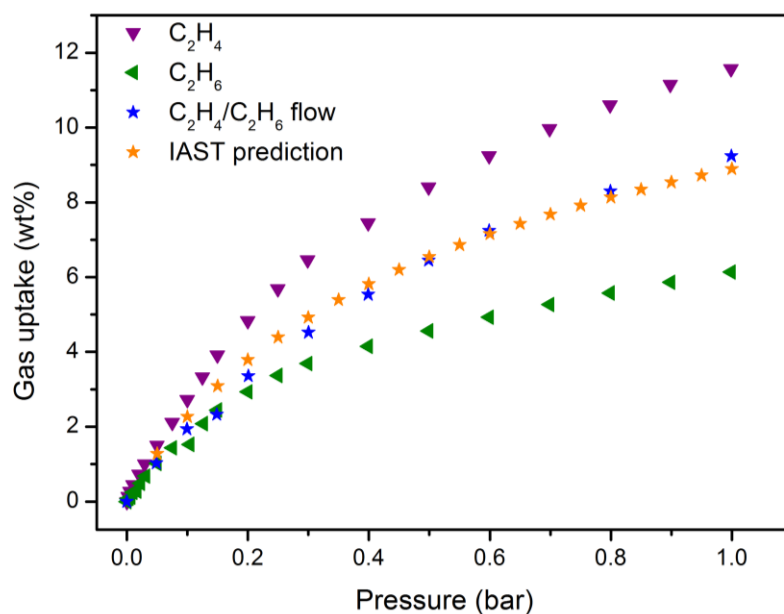
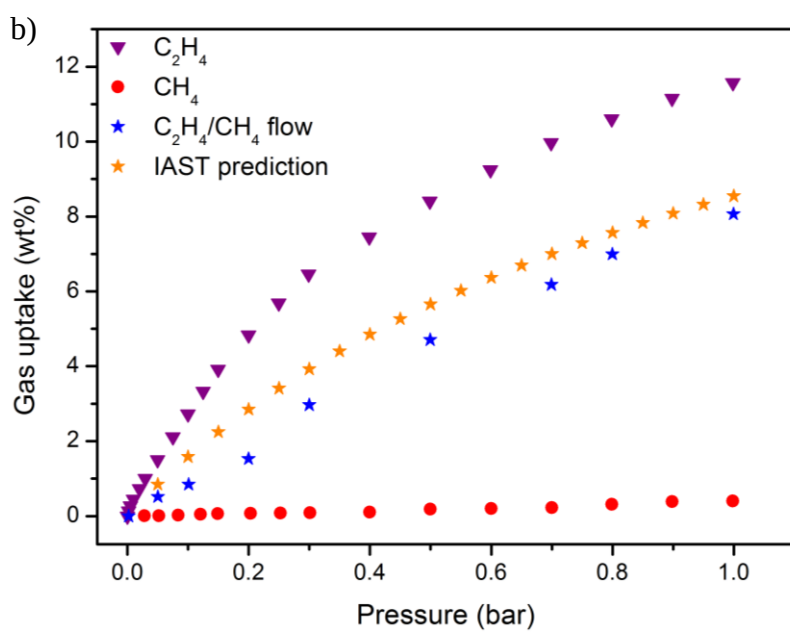
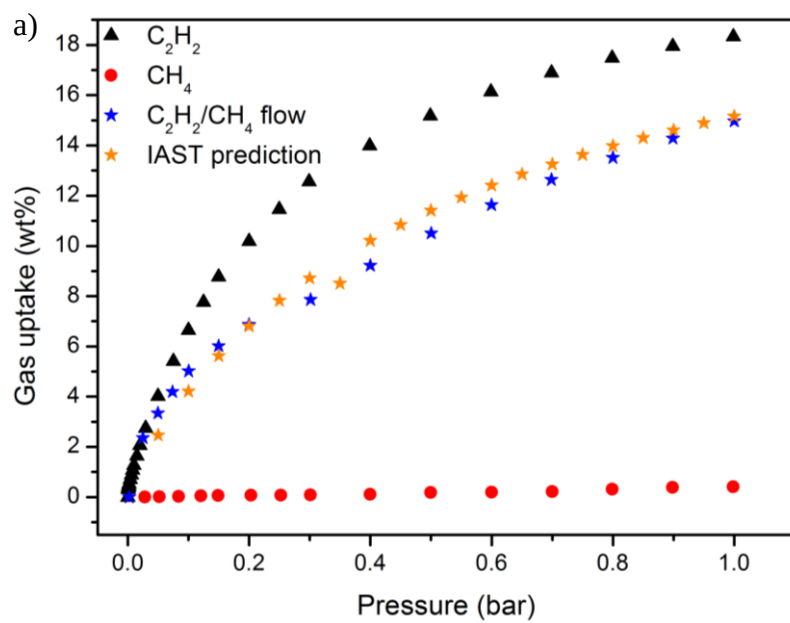


Fig. 4.13 Dual component adsorption isotherm for a 1:1 C₂H₄/C₂H₆ mixture at 293 K from 0 to 1 bar in NOTT-300(Al).

NOTT-300(Al) displays exceptional C₂/C₁ hydrocarbon selectivity; this is owing to the very low CH₄ uptakes observed < 1 wt% at 293 K and 1 bar. All the C₂/C₁ hydrocarbon dual component adsorption isotherms clearly show this high calculated selectivity is real, (Fig. 4.14). The IAST prediction model matches well with the experimental uptakes recorded in all C₂/C₁ mixtures except for C₂H₆/CH₄ where the recorded uptake is much higher than the prediction. The experimental uptake for the C₂H₆/CH₄ mixture is 5.9 wt%, which matches very closely to the uptake of pure C₂H₆ at 293 K and 1 bar, 6.1 wt%.



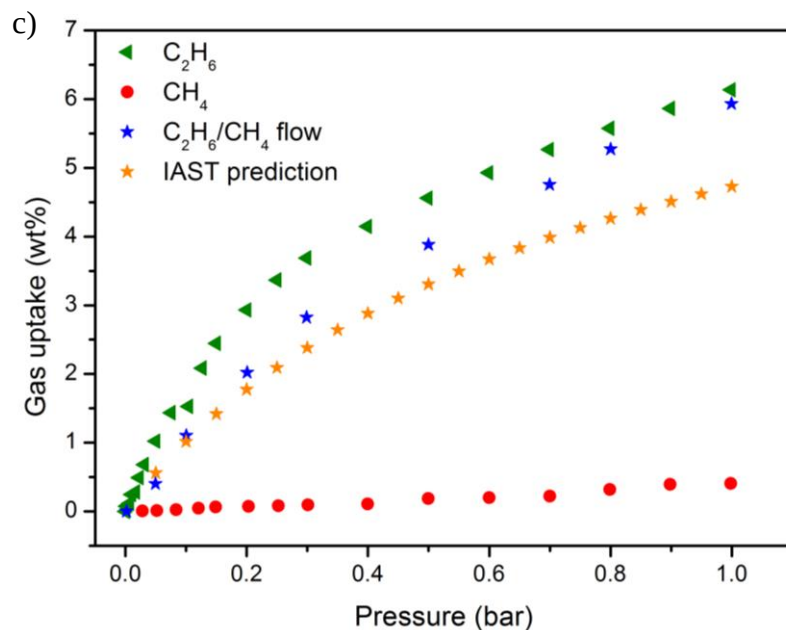


Fig. 4.14 Dual component adsorption isotherm at 293 K from 0 to 1 bar in NOTT-300(Al) for C₂/C₁ hydrocarbon mixtures **a)** C₂H₂/CH₄ **b)** C₂H₄/CH₄ and **c)** C₂H₆/CH₄.

4.2.6.2 Dual Component Adsorption Isotherms for NOTT-300(AlCr2:1)

Dual component adsorption isotherms were carried out for three different C₂ hydrocarbon mixtures in AlCr2:1 at 293 K (C₂H₂/C₂H₄, C₂H₂/C₂H₆ and C₂H₄/C₂H₆). The selectivity calculations revealed that AlCr2:1 showed no preferential adsorption of either C₂H₄ or C₂H₆, the single component adsorption isotherms displayed similar uptakes for both gases, 13.5 wt% and 12.2 wt% respectively further reinforcing the lack of selectivity. The C₂H₄/C₂H₆ dual component adsorption isotherm confirms the absence of selectivity in AlCr2:1 that was calculated (Fig 4.15). The IAST prediction matches well with the experimental uptakes recorded, illustrating the compatibility of the two techniques used. NOTT-300(Al) displayed reasonable selectivity for C₂H₄ over C₂H₆, which is not maintained in AlCr2:1. The reason for this is likely to be the

slight increase in pore size, meaning the diffusion of C_2H_6 is less restricted and able to travel along the channel with a lower energy barrier. There are also no open metal sites within the framework that would selectively adsorb the alkene over the alkane. The main interactions formed between the adsorbed gas and NOTT-300 materials are H-bonds which are further reinforced by van der Waals interactions. The differences in the strength of these interactions between the framework and C_2H_4 and C_2H_6 are likely to be small.

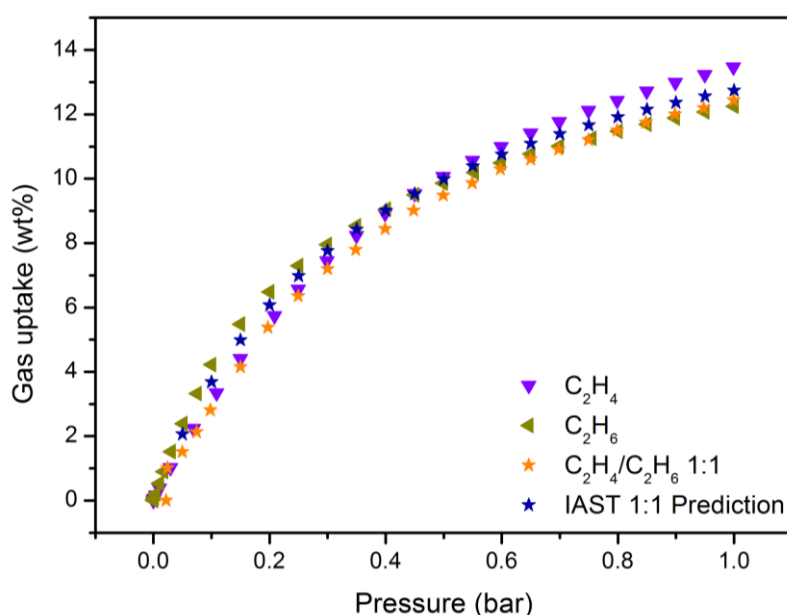


Fig. 4.15 Dual component adsorption isotherm for a 1:1 C_2H_4/C_2H_6 mixture at 293 K from 0 to 1 bar in AlCr2:1.

The dual component adsorption isotherm recorded for the C_2H_2/C_2H_4 mixture shows more promise in terms of separation ability/selectivity. The experimental uptake recorded reached 16.57 wt% at 293 K and 1 bar, matching closely with the IAST prediction of 16.3 wt%. There is a larger difference in uptake of the two single gases compared with C_2H_4/C_2H_6 , as shown by the single component adsorption (Fig. 4.16). The corresponding C_2H_2 uptake at 0.5 bar is 15.1 wt%, whereas C_2H_4 only reaches 10.1 wt% under these same conditions. The IAST

calculated selectivity for this mixture of gases is 2.1 at 293 K, therefore, the gas adsorbed in the dual component adsorption isotherm is likely a mix of the two gases but consisting of more C_2H_2 than C_2H_4 , showing an element of selectivity.

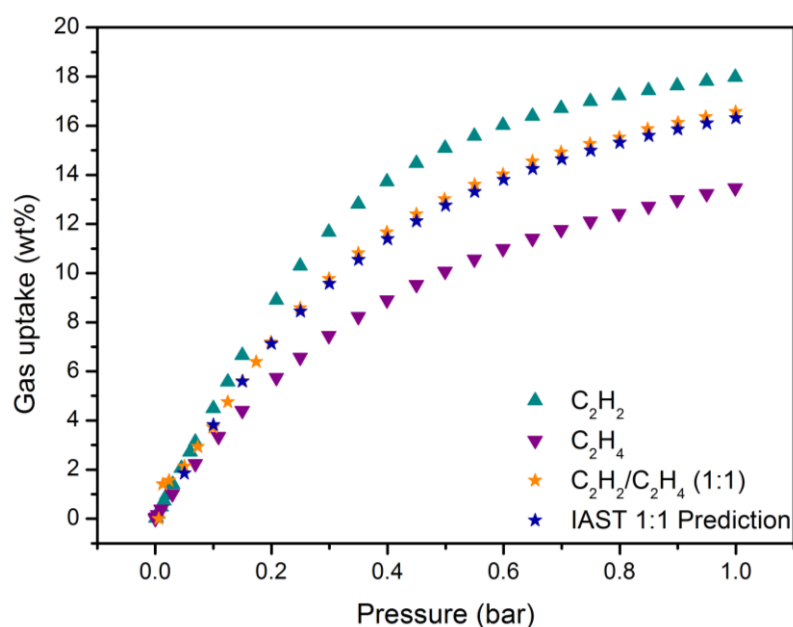


Fig. 4.16 Dual component adsorption isotherm for a 1:1 C_2H_2/C_2H_4 mixture at 293 K from 0 to 1 bar in $AlCr_2:1$.

The highest selectivity calculated for possible C_2 hydrocarbon mixtures in $AlCr_2:1$ was for the C_2H_2/C_2H_6 separation. This is because the C_2H_2 molecules can interact more strongly with the framework than C_2H_6 through a combination of stronger H-bonds, van der Waals interactions and π - π stacking interactions with the phenyl rings in the ligand. The dual component adsorption isotherm supports this (Fig. 4.17), as the recorded uptake at 1 bar is 16.3 wt% and this high uptake (higher than that for C_2H_6 at 1 bar and 293 K) is indicative of mainly C_2H_2 adsorption.

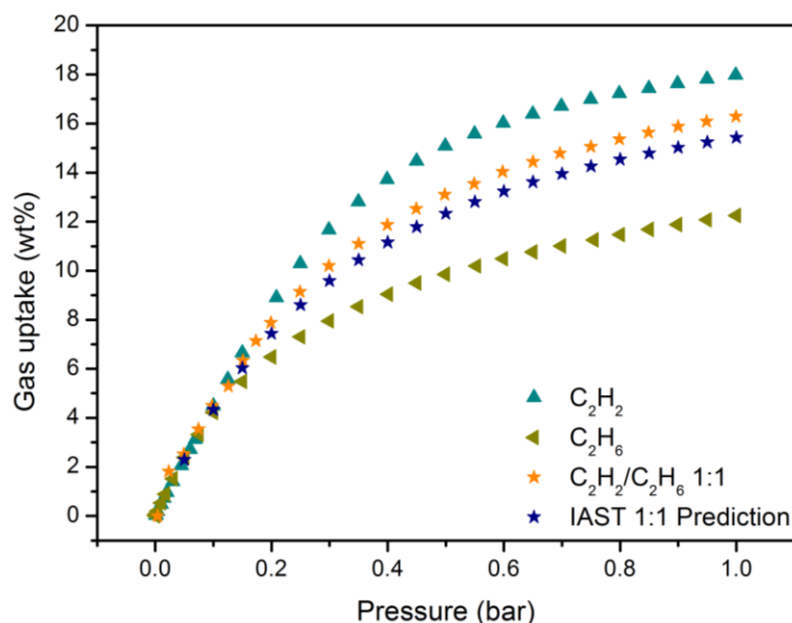


Fig. 4.17 Dual component adsorption isotherm for a 1:1 C₂H₂/C₂H₆ mixture at 293 K from 0 to 1 bar in AlCr₂:1.

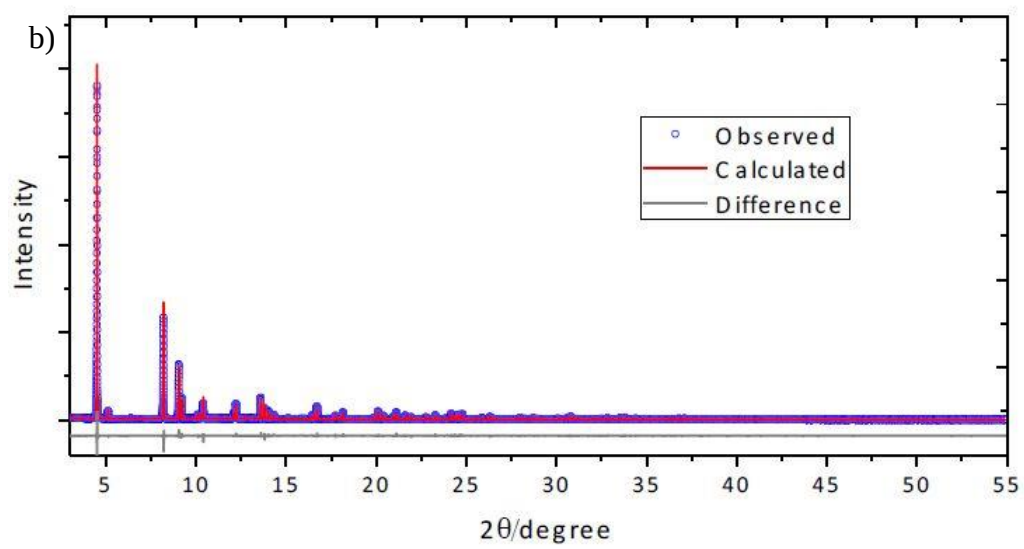
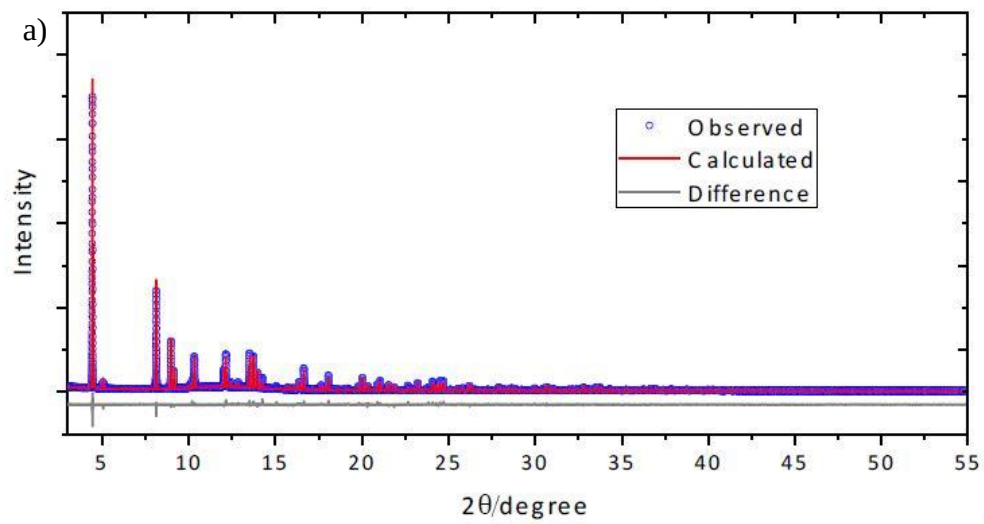
The combination of IAST calculations and predictions and experimental dual component adsorption isotherms works well for displaying the practical selectivity of these materials. The moderate C₂H₄/C₂H₆ separation shown by NOTT-300(Al) is lost in AlCr₂:1 as the diffusion of C₂H₆ has a lower energy barrier as the pores are larger in AlCr₂:1. The C₂H₂/C₂H₄ and C₂H₂/C₂H₆ selectivity is lower in AlCr₂:1 than in NOTT-300(Al) but AlCr₂:1 still shows the potential to separate these gas mixtures as these separation processes are based more on the thermodynamic separation than a difference in kinetics.

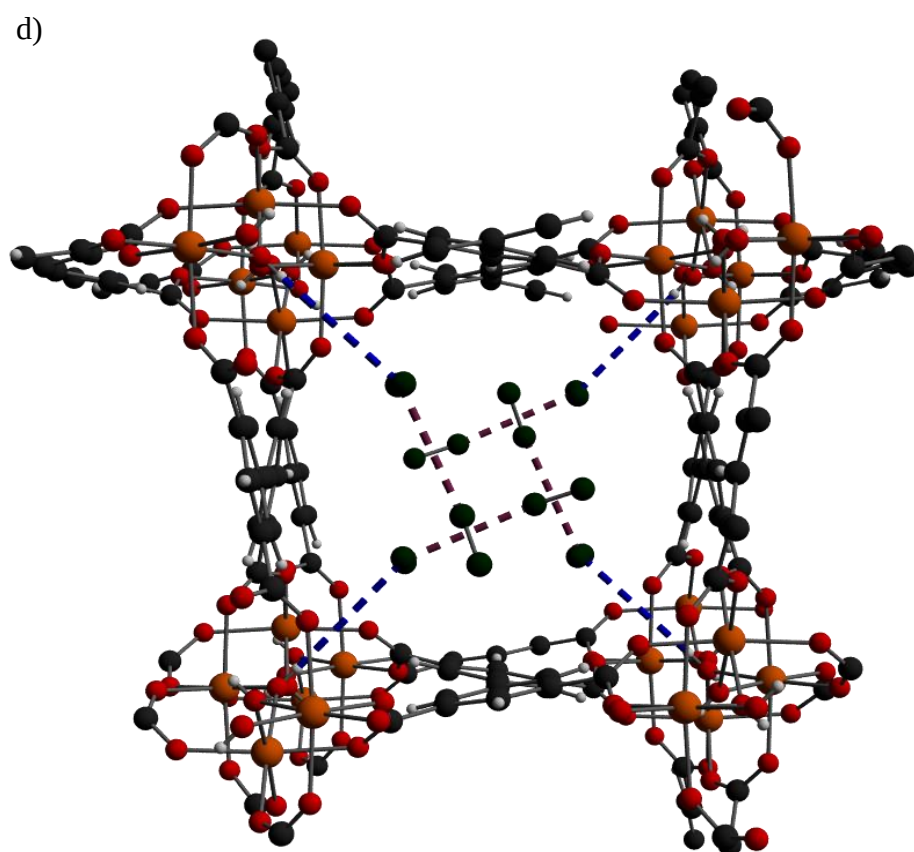
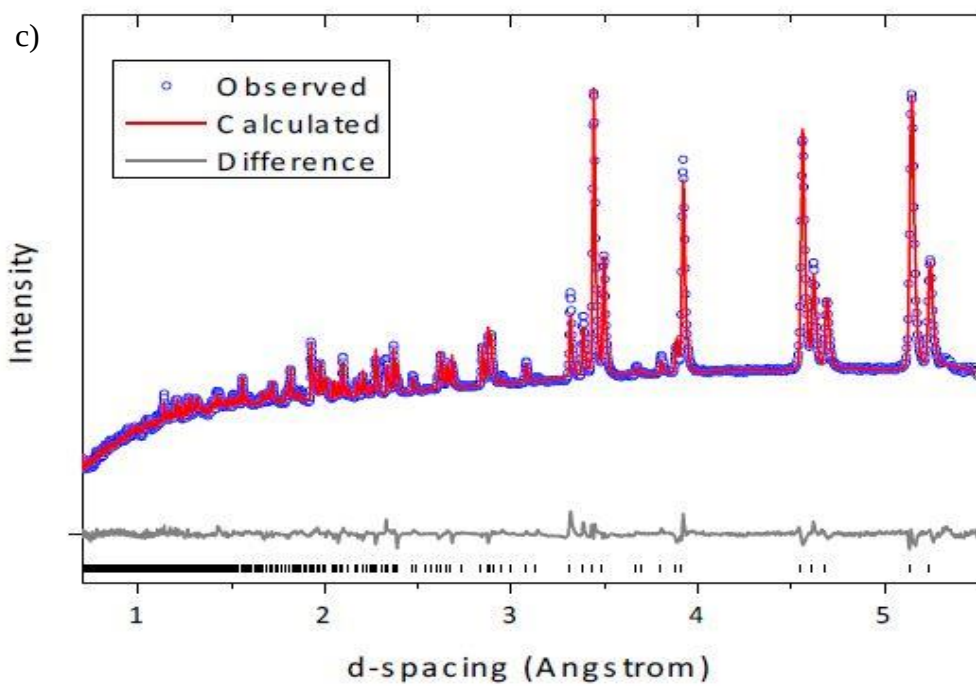
4.2.7.1 C₂-Loaded PXRD and INS Studies on NOTT-300(Al)

A combination of *in situ* gas loaded PXRD and inelastic neutron spectroscopy (INS) was used in order to probe the adsorption sites and the dynamics of the adsorption process of the C₂ hydrocarbons in NOTT-300(Al). The combination

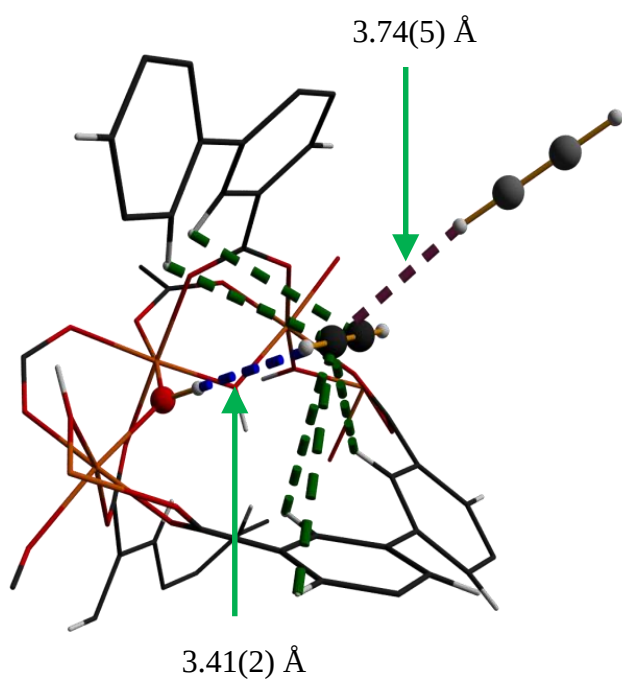
of these two experimental techniques has been previously used to probe the dynamics of CO₂ binding within NOTT-300(Al) with great success. After refinement of the PXRD data (Fig. 4.18 a-c) two distinct adsorption sites were found, site (I) and site (II) (Fig. 4.18d) both molecules are located at general positions and as a result positional disorder of the molecules is observed. At site (I) both C₂H₂ and C₂H₄ bind in a side on fashion with the bridging –OH group *via* the formation of H-bonds. The interaction between the framework and the adsorbed gas is strongest for C₂H₂, as shown by the shorter OH...C distance: 3.41(2) Å for C₂H₂, 3.72(6) Å for C₂H₄ and 3.84(9) Å for C₂H₆. Site (I) is further stabilised by the addition of supramolecular interactions, van der Waals, between the aromatic protons and the unsaturated C-C bond and π - π stacking interactions to the phenyl rings of the ligand. These supramolecular interactions are in the range of 2.9 – 4.9 Å for all C₂ hydrocarbons; these act as a support and are not the dominant interaction between the gas and the framework, hence they are similar for all the gases.

The second site (site (II)) is located in the middle of the pore and interacts primarily with the gas molecules at the first site *via* intermolecular dipole interactions. The position of site II is also further stabilised by van der Waals and π - π stacking interactions. The distance between site (I) and site (II) is shorter in C₂H₄-loaded NOTT-300(Al) than for C₂H₂-loaded NOTT-300(Al), 3.52(8) Å vs. 3.74(5) Å. The binding strength, assessed by the length of the H-bond, of the C₂ hydrocarbons follows the trend C₂H₂ > C₂H₄ > C₂H₆ as expected.

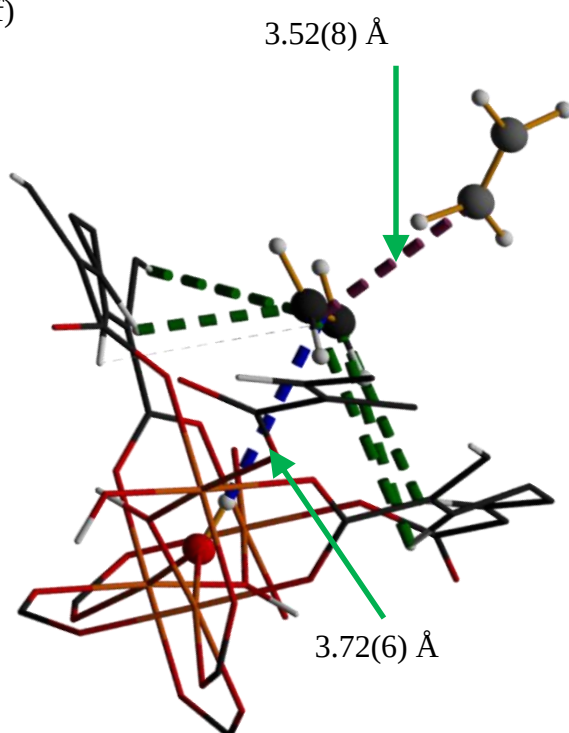




e)



f)



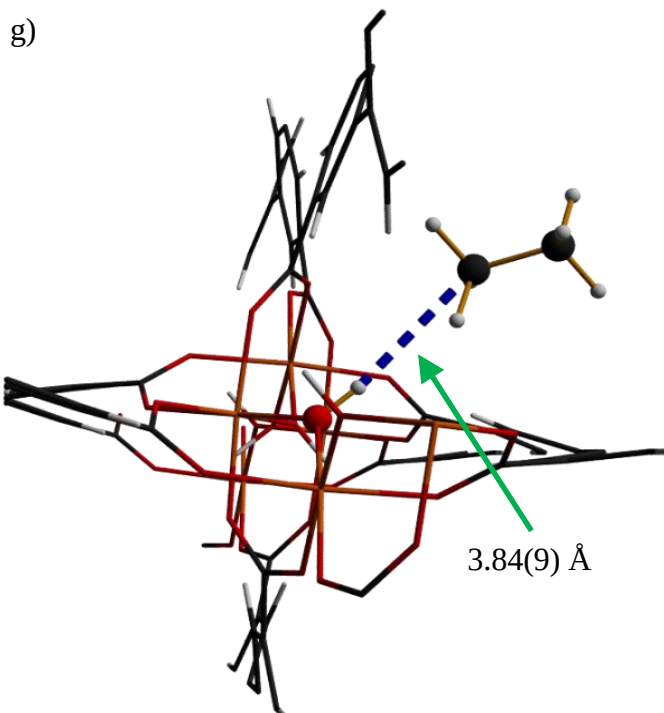


Fig. 4.18 PXRD patterns [observed (blue), calculated (red) and difference (grey)] for the Rietveld refinement of **a)** C₂H₂-loaded NOTT-300(Al), **b)** C₂H₄-loaded NOTT-300(Al) and **c)** C₂H₆-loaded NOTT-300(Al) λ - 0.825633. **d)** Views of the structure of C₂-loaded NOTT-300(Al) obtained from PXRD with the positional disorder removed for clarity. (Al – orange, oxygen – red, carbon – grey, hydrogen – white). General view of adsorbed unsaturated C₂ hydrocarbons in the pore channel to show the two adsorption sites. **e)** Detailed view of C₂H₂ interaction with the framework [OH $\cdots$ C = 3.41 Å], **f)** Detailed view of the C₂H₄ interaction with the framework [OH $\cdots$ C = 3.72 Å] **g)** View of the C₂H₆ interaction with the framework [OH $\cdots$ C = 3.84 Å]. The adsorbed C₂ molecules and μ_2 -OH groups are highlighted in ball and stick mode. C₂H_x(II) is highlighted in light grey. The H-bonds between C(δ^-) of C₂H_x and H(δ^+) from the -OH group is highlighted in blue, dipole interactions between sites (I) and (II) are highlighted in purple and van der Waals interactions between aromatic hydrogens and sites (I) and (II) are highlighted in green [CH $\cdots$ C $\equiv$ C 2.9 – 4.9 Å].

For INS data collection the sample has to be cooled to below 7 K to minimise the thermal motion of the framework host and adsorbed gas. Initially a series of spectra were recorded for bare NOTT-300(Al), solid C₂H₂, solid C₂H₄ and solid

C_2H_6 , thus any changes to the framework or the hydrocarbon species upon adsorption could be observed, Fig. 4.19.

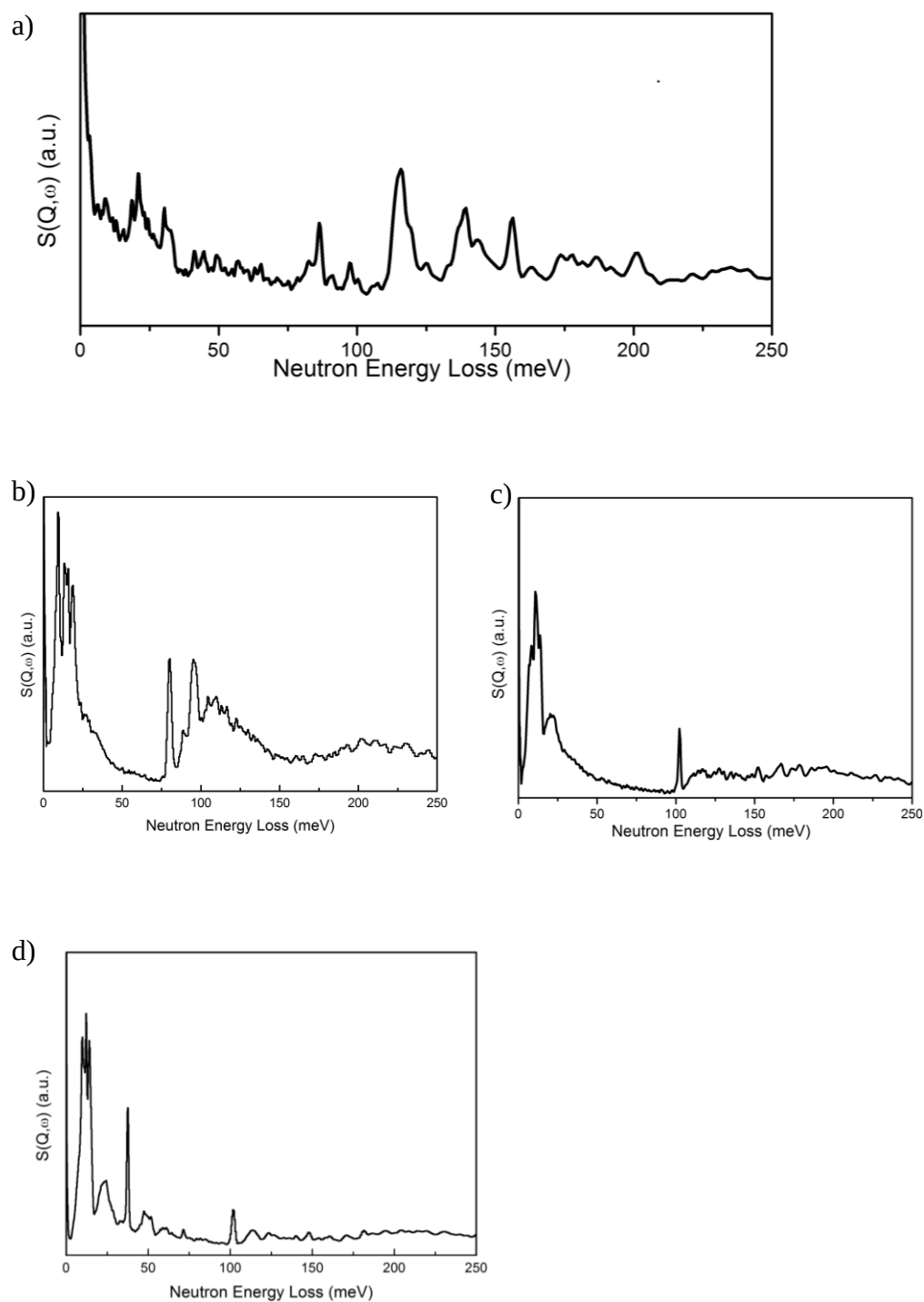
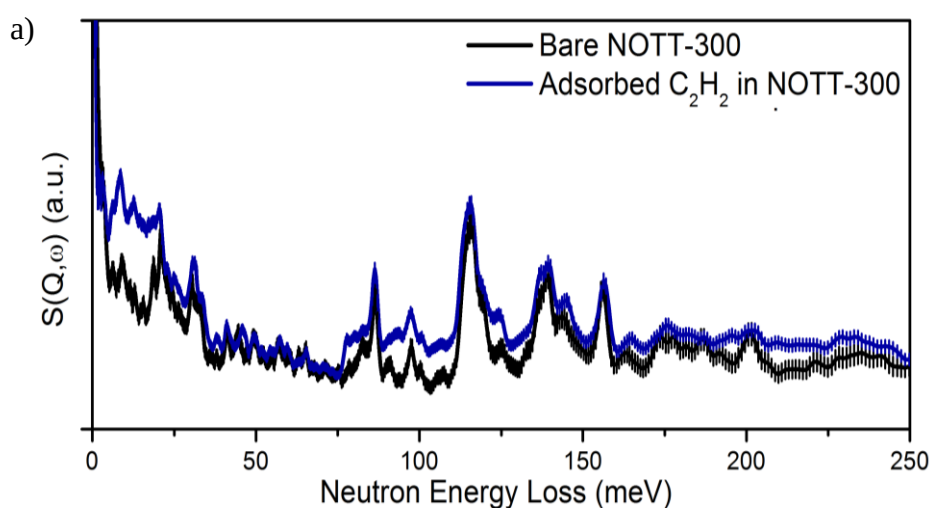


Fig. 4.19 INS spectrum of **a)** bare NOTT-300(Al), **b)** solid C_2H_2 , **c)** solid C_2H_4 and **d)** solid C_2H_6 .

Upon loading of C_2H_2 five major peak changes can be observed, I and II occur at low energy transfer (5 – 24 and 25 – 50 meV, respectively) and III, IV and V occur at higher energy loss (80, 95 and 120 meV, respectively) (Fig. 4.20). Based on the solid C_2H_2 spectra peaks I, III and IV can be assigned to translational, asymmetric and symmetric C-H vibrational modes in C_2H_2 . Both peaks III and IV appear as doublets in the C_2H_2 -loaded MOF compared to singlets in the solid C_2H_2 spectra. This indicates a loss of degeneracy of the C-H vibrational modes when C_2H_2 interacts with the framework host *via* its π electron system. Peaks II is assigned as the –OH groups bending perpendicular to the Al-O-Al plane and peak V is assigned to the bending and the out of plane wagging of the aromatic CH groups adjacent to the C_2H_2 . There are large changes in these peaks (II and V) suggesting the adsorbed C_2H_2 has a direct interaction with these groups, which is in good agreement with the adsorption sites found by PXRD.



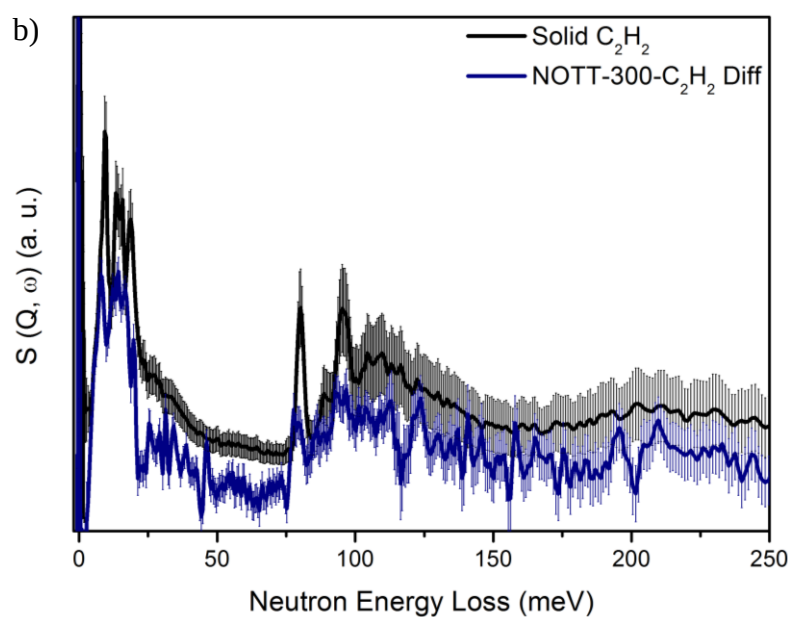
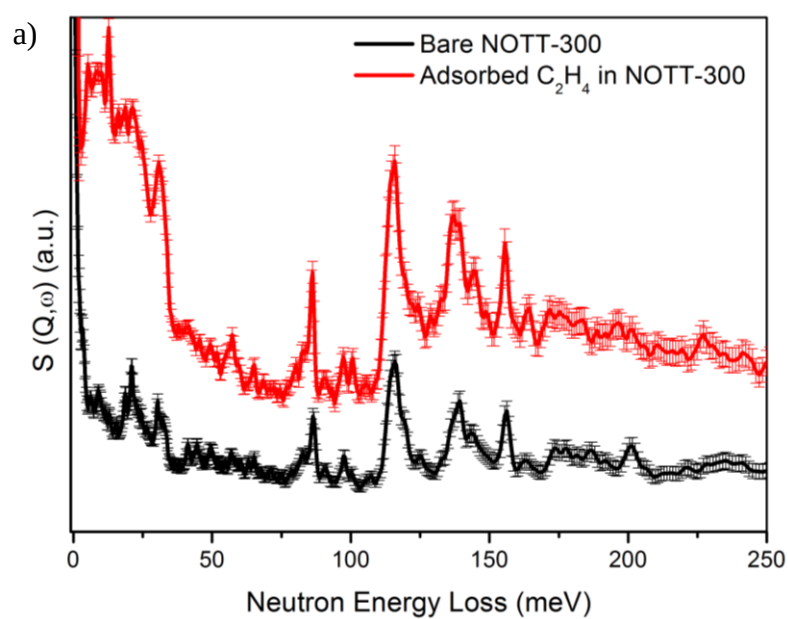


Fig. 4.20 INS spectra **a)** comparison of bare and C_2H_2 -loaded NOTT-300(Al) **b)** comparison of the difference spectrum of adsorbed C_2H_2 and solid C_2H_2 .

The C_2H_4 loaded INS data (Fig. 4.21) is quite different to that for C_2H_2 , with a large broad peak below 25 meV and no other distinct energy transfer peaks. This is characteristic of one dimensional recoil rotational motion of C_2H_4 molecules along its C=C axis.



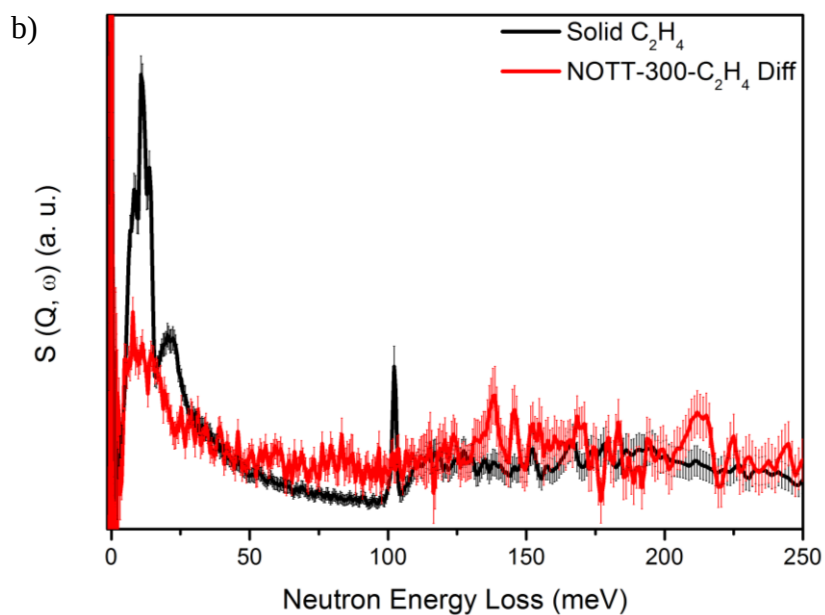
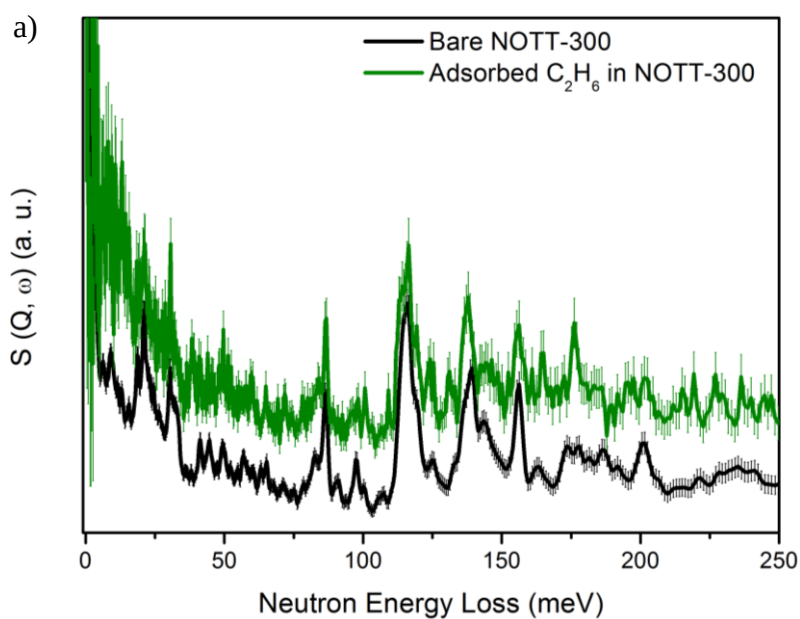


Fig. 4.21 INS spectra **a)** comparison of bare and C_2H_4 -loaded NOTT-300(Al) **b)** comparison of the difference spectrum of adsorbed C_2H_4 and solid C_2H_4 .

The INS spectra of C_2H_6 loaded NOTT-300(Al) displays only one broad peak at low energy transfer and is assigned to the one dimensional rotational motion along the C-C axis (Fig. 4.22).



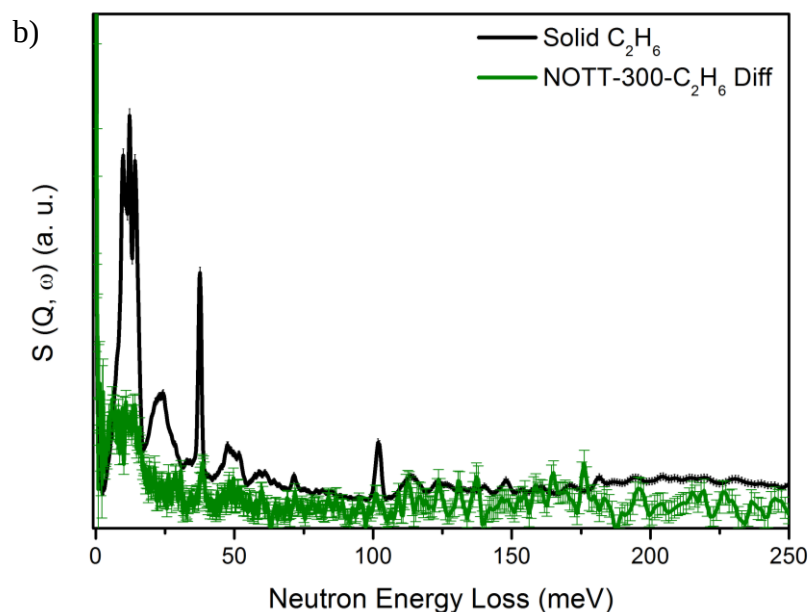


Fig. 4.22 INS spectra **a)** comparison of bare and C_2H_6 -loaded NOTT-300(Al) **b)** comparison of the difference spectrum of adsorbed C_2H_6 and solid C_2H_6 .

DFT calculations were used to simulate the INS spectra and to optimise the structures. The cif files obtained from the PXRD data were used in this process and the experimental spectra showed excellent agreement with the spectra derived from the DFT calculations.

Both the PXRD data and INS calculations show that C_2H_2 binds the strongest within the host, the binding of C_2H_4 and C_2H_6 was not sufficiently strong enough to cause an observable change in the INS spectra.

4.2.7.2 C_2H_2 -Loaded *In Situ* PXRD Studies on NOTT-300(Cr)

In order to further investigate the C_2H_2 adsorption in NOTT-300(Cr) *in situ* synchrotron PXRD experiments were carried out. The diffraction data were analysed by using Rietveld refinements (Fig. 4.23) based on the crystal structure

model of NOTT-300(Cr) and two distinct adsorption sites were found within the framework, C₂H₂(I) and C₂H₂(II).

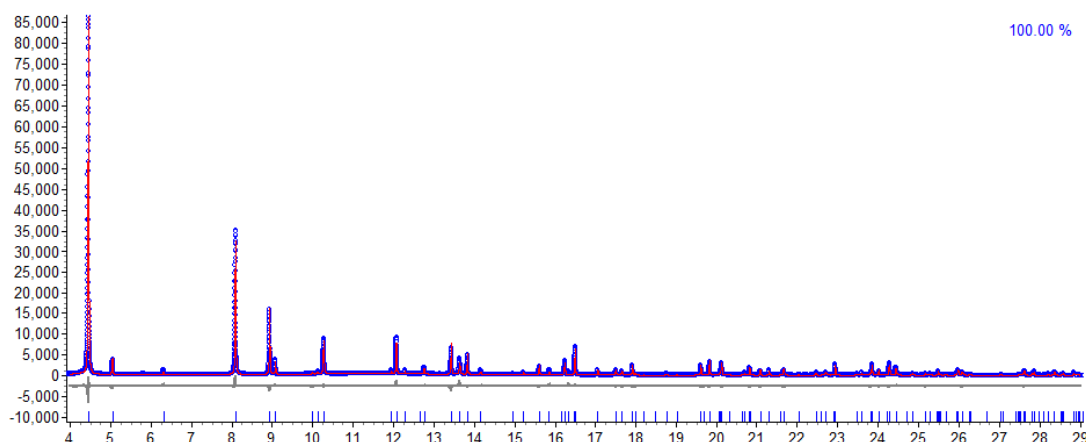


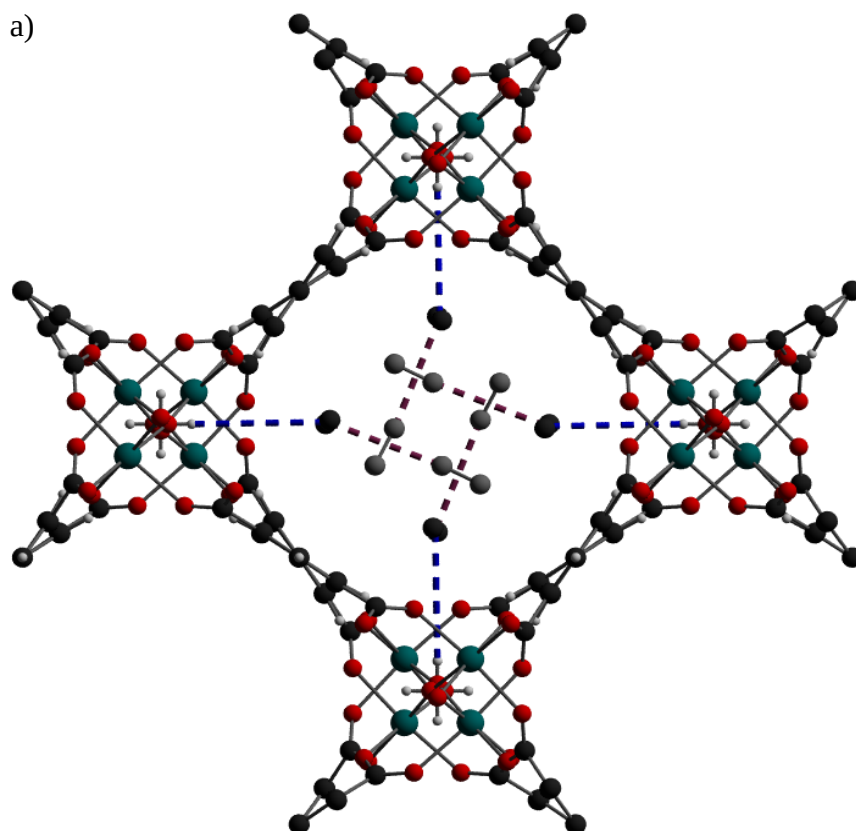
Fig. 4.23 PXRD patterns [observed (blue), calculated (red) and difference (grey)] for the Rietveld refinement of C₂H₂-loaded NOTT-300(Cr).

The first C₂H₂ molecule (C₂H₂(I)) interacts predominantly with the bridging -OH group (Fig. 4.24) in a side on fashion *via* the formation of H-bonds between the δ^+ H and the electron rich π system of C $\equiv$ C (O-H $\cdots$ C(10) $\equiv$ C – 3.93(4) Å, O-H $\cdots$ C(11) $\equiv$ C – 3.62(4) Å). The C₂H₂ molecules exhibit positional disorder and as such the occupancy of each site approaches 0.5 at 1 bar, this is in keeping with the C₂H₂ adsorption at 1 bar. The side on binding of the C₂H₂ molecule means the C₂H₂ is parallel with the phenyl rings in the ligand allowing for further cooperative binding through van der Waals interactions and π - π stacking interactions between the adsorbed gas and the phenyl rings (Fig. 4.24). These weaker van der Waals interactions are in the range of 3.03(6) – 4.34(8) Å (C-H $\cdots$ C $\equiv$ C). C₂H₂(II) interacts mainly with C₂H₂(I) in a bent T-shape through electrostatic dipole interactions (C $\equiv$ C(10) $\cdots$ C(7) $\equiv$ C – 3.32(6) Å, C $\equiv$ C(11) $\cdots$ C(7) $\equiv$ C – 3.42(4) Å). The position of C₂H₂(II) is further stabilised

through weaker van der Waals interactions between the aromatic –CH and the π electron system of $\text{C}\equiv\text{C}$ in the range of $3.83(4) - 4.66(5)$ Å, ($\text{C-H}\cdots\text{C}\equiv\text{C}$).

There also appears to be further interactions between the $\text{C}_2\text{H}_2(\text{II})$ molecules, $\sim 3 - 4$ Å, almost forming a chain of adsorbed C_2H_2 along the channel and representing an efficient packing mode of C_2H_2 where one molecule can stabilise the adjacent C_2H_2 in the chain. However, this is not observed with CO_2 adsorption in the framework.

The strong adsorption affinity displayed by NOTT-300(Cr) for C_2H_2 is due to the cumulative effect of several weak interactions, H-bonds, van der Waals and π - π stacking. Although these interactions are weaker than those formed between C_2H_2 molecules and open metal sites, the combination of weak to moderate supramolecular interactions work together to encourage adsorption of C_2H_2 .



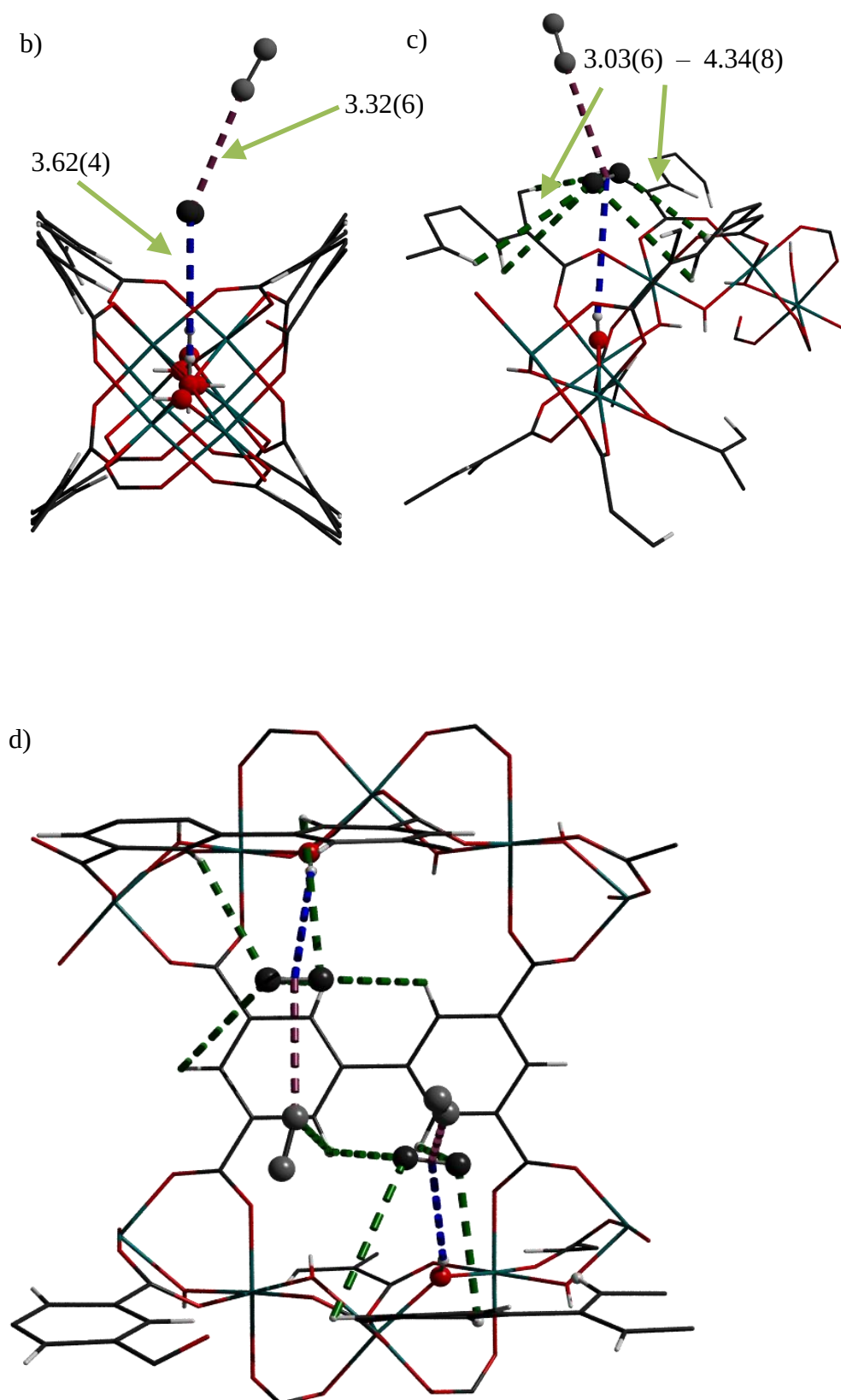


Fig. 4.24 Views of the structure of C₂H₂- loaded NOTT-300(Cr) obtained from PXRD with positional disorder removed for clarity. (Cr - teal, oxygen - red, carbon - grey, hydrogen -

white). **a)** View of adsorbed C₂H₂ in the pore channel. C₂H₂(II) highlighted in light grey. The H-bonds between C(δ^-) of C₂H₂ and H(δ^+) from the –OH group is highlighted in blue, [C $\cdots$ H = 3.62 Å], dipole interactions between C₂H₂ (I) and (II) are highlighted in purple [C $\equiv$ C $\cdots$ C₂H₂ = 3.32 Å] and van der Waals interactions between aromatic hydrogens and C₂H₂ (I) and (II) are highlighted in green [CH $\cdots$ C $\equiv$ C 3.03 – 4.34 Å]. **b)** Detailed view of O-H $\cdots$ C $\equiv$ C H-bonds, **c)** View of cooperative/assistive van der Waals interactions between aromatic hydrogens and C₂H₂ (I). **d)** Detailed view of C₂H₂ (I) and C₂H₂ (II) dipole interaction and additional van der Waals interactions between adsorbed gas and framework (distances not included for clarity). The adsorbed C₂H₂ molecules and μ_2 -OH groups are highlighted in ball and stick mode.

4.2.8 C₂ Hydrocarbon Separation in NOTT-300(Al) by Breakthrough Experiments

A series of breakthrough experiments were performed on NOTT-300(Al) using different mixtures of C₂ hydrocarbons, C₂H₂/C₂H₄ and C₂H₄/C₂H₆, at 293 K. An equimolar mixture of hydrocarbon was flowed over a fixed bed of NOTT-300(Al) and the exiting gas stream analysed by mass spectrometry. Previous selectivity calculations and mixed component adsorption isotherms suggest that NOTT-300(Al) is capable of selectively adsorbing and separating C₂ hydrocarbon mixtures.

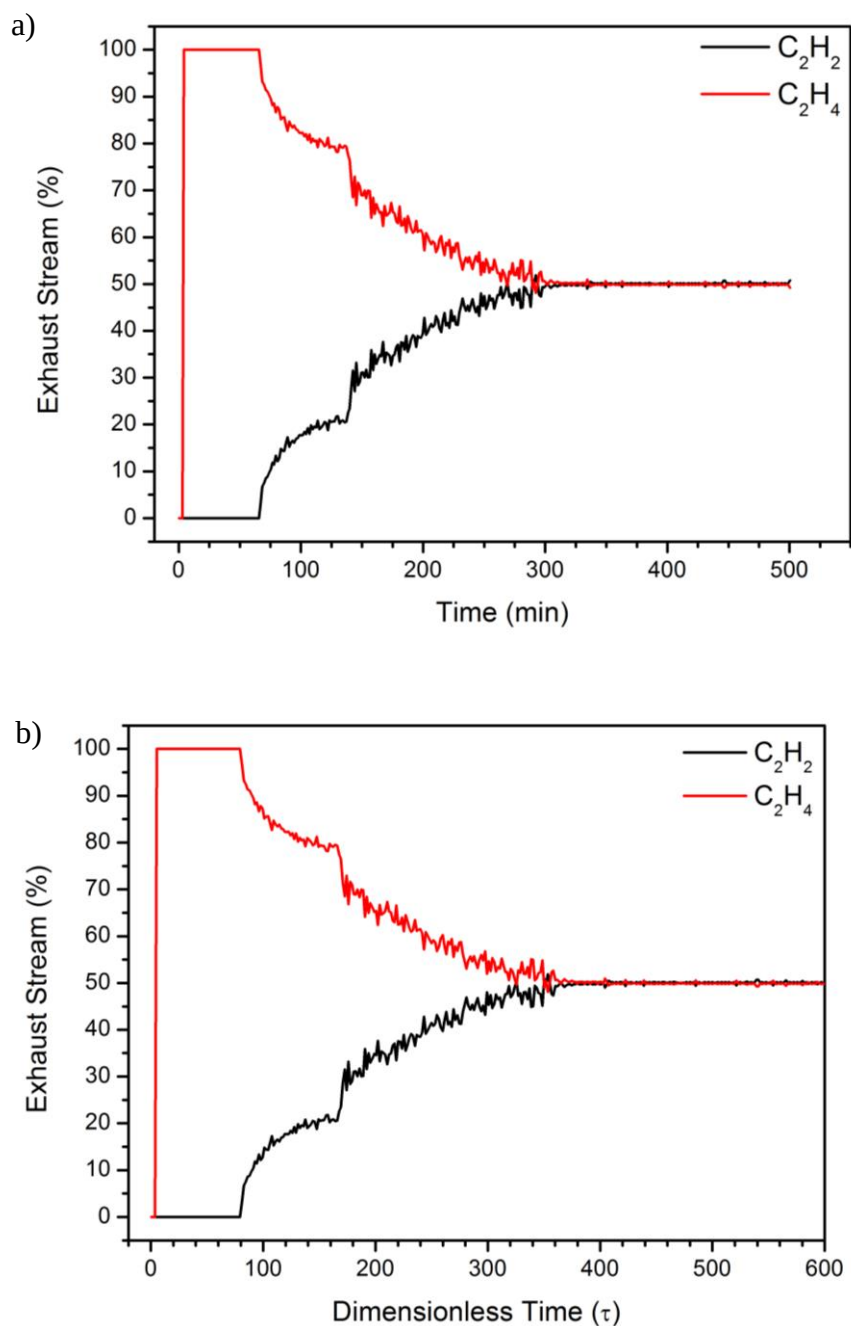


Fig. 4.25 Breakthrough adsorption curve for a C_2H_2/C_2H_4 mixture in NOTT-300(Al) at 293 K shown in **a)** real time and **b)** dimensionless time.

The calculated IAST selectivity for C_2H_2/C_2H_4 in NOTT-300(Al) at 293 K is 4.3 and *in situ* INS and PXRD studies show that C_2H_2 interacts more strongly with the material compared with C_2H_4 through a combination of stronger H-bonds and π - π stacking with the phenyl rings. This is also clearly shown by the difference in the heat of adsorption between the two gases ($\sim 26 \text{ kJ mol}^{-1}$ vs. ~ 22

kJ mol^{-1}). The breakthrough experiments also confirm this, as C_2H_4 eluted from the sample first whereas C_2H_2 was retained, Fig. 4.25. The C_2H_4 stream remained pure until C_2H_2 was first detected at ~ 65 mins. This initial C_2H_2 detection plateaued at $\sim 20\%$ until further breakthrough occurred at ~ 135 mins. The C_2H_2 amount then slowly increased to 50% at ~ 300 mins as the sample had reached saturation. This shows that from an equimolar mixture NOTT-300(Al) has the ability to purify C_2H_4 to $>99\%$ because of the different strengths in interaction between the adsorbed gas and the framework.

The IAST selectivity for $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ for NOTT-300(Al) is 3.1 and the dual component adsorption isotherms confirm the high selectivity, showing preferential adsorption and increased adsorption capacity of C_2H_4 over C_2H_6 . Therefore it is assumed NOTT-300(Al) would separate C_2H_4 and C_2H_6 mixtures by removing C_2H_4 from the gas stream. However this was not seen in the breakthrough curve (Fig. 4.26), instead C_2H_4 was detected first while C_2H_6 was retained in the framework. A pure C_2H_4 stream was maintained for ~ 35 mins when C_2H_6 broke through and was detected (45 mins). This is likely because of the difference in kinetics of the two different gases in the channels of the MOF.²¹ The diffusion of C_2H_6 is much slower than C_2H_4 and so the process is a kinetic separation, not a thermodynamic process like the separation of $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$.

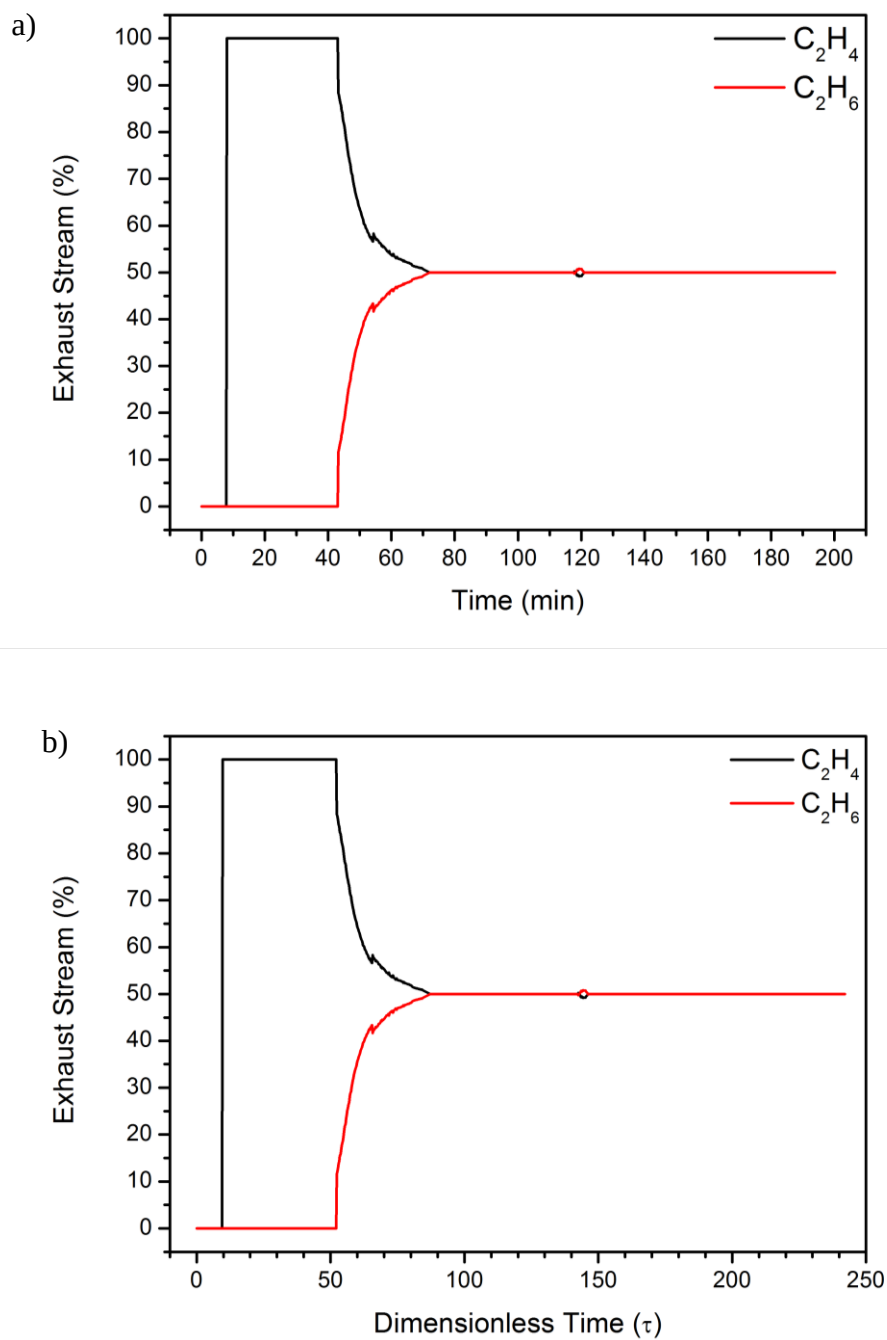


Fig. 4.26 Breakthrough adsorption curve for a C_2H_2/C_2H_4 mixture in NOTT-300(Al) at 293 K shown in **a)** real time and **b)** dimensionless time.

These breakthrough experiments show that NOTT-300(Al) is capable of separating both C_2H_2/C_2H_4 and C_2H_4/C_2H_6 mixtures through either a) preferential adsorption of one gas over the other due to stronger interactions with the framework material, or b) through a kinetic process where the diffusion of

one gas through the channel is quicker than the other. This is further supported when using dimensionless time (Fig. 4.25b and 4.26b), as the long separation time is maintained showing that the behaviour observed is a property of the material and not because of the sample bed length.

4.3 Conclusion

The adsorption capacity and the potential for selectivity for the C₂ hydrocarbons in NOTT-300(Al,Cr) materials was investigated and it was found that all materials possess the ability to separate C₂H₂ from C₂H₂/C₂H₄ and C₂H₂/C₂H₆ mixtures as shown by IAST calculations and dual component adsorption isotherms. The *in situ* gas loaded PXRD studies confirmed the reason for this selectivity as there are several weak/moderate interactions working cooperatively to stabilise C₂H₂ within the pores and drive adsorption. These cooperative interactions consist of H-bonds, van der Waals interactions and π - π stacking interactions. The C₂H₄/C₂H₆ selectivity was much lower in the Cr containing NOTT-300 frameworks, NOTT-300(Cr), AlCr₂:1, AlCr₁:1 and AlCr₂:3, with no preferential adsorption observed for either gas. However, NOTT-300(Al) displays great C₂H₄/C₂H₆ selectivity owing to the differences in the kinetics of the gases within the channel, C₂H₆ diffuses much slower than C₂H₄, and this property is lost in the Cr containing materials owing to the slight increase in pore size.

A combination of *in situ* PXRD and INS studies on NOTT-300(Al) shows that C₂H₂ interacts more strongly within the framework than either C₂H₄ or C₂H₆. This will likely be a contributing factor for the moderate C₂H₂/C₂H_x selectivity.

Dual component adsorption isotherms were used in conjunction with the IAST selectivity calculations in order to show the selectivity of both NOTT-300(Al) and AlCr₂:1 in practical applications. It was shown that these techniques work well together, with the IAST selectivity matching the dual component adsorption uptakes quite well. It was shown the NOTT-300(Al) displays greater selectivity in all gas mixtures studied, the greatest difference being the C₂H₄/C₂H₆ selectivities. These techniques also clearly displayed the exceptional C₂/C₁ hydrocarbon selectivity shown by NOTT-300(Al). The Cr containing NOTT-300 materials displayed great C₂/C₁ hydrocarbon selectivity, however, not as high as that shown by NOTT-300(Al) owing to the very low CH₄ uptake observed in NOTT-300(Al).

Breakthrough experiments allow us to see how well the selectivity translates to real world separations of gas mixtures. The two breakthrough experiments performed in this chapter clearly show that NOTT-300(Al) has the ability to separate C₂ hydrocarbon mixtures through either a thermodynamic process (C₂H₂/C₂H₄) or a kinetic a process (C₂H₄/C₂H₆).

There is great potential for future work in this area, for instance, breakthrough experiments on all the mixed metal materials would help to give an insight into their separation ability. One drawback for this method, however, is it requires a relatively large amount of sample (> 1.5 g) which is difficult to synthesise for the mixed metal materials and NOTT-300(Cr).

The unusual adsorption behaviour displayed by AlCr₂:3, increased adsorption with increase in temperature, could prove to be interesting if investigated further and proved to be real. The hysteresis observed in several of the gas sorption

isotherms for AlCr1:1 and AlCr2:3 should be further investigated to locate the source.

Dual component adsorption isotherms of different C₂ and C₂/C₁ hydrocarbon mixtures in NOTT-300(Cr), AlCr(1:1) and AlCr(2:3) could also provide some interesting results as all the materials possess different selectivities.

4.4 References

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Chapter 5 - Experimental

All chemicals were used as purchased without further purification. Biphenyl-3,3',5,5'-tetracarboxylic acid (H_4L^1) used for the MOF syntheses was purchased from Manchester Organics (Fig. 5.1).

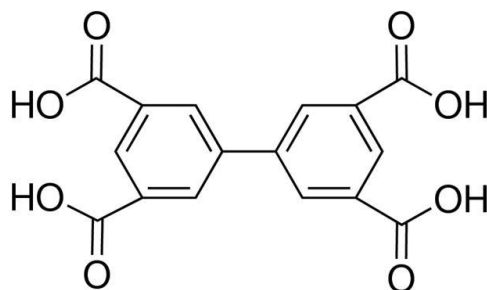


Fig. 5.1 Structure of H_4L^1 used in the synthesis of NOTT-300 frameworks.

5.1 MOF Synthesis

5.1.1 Synthesis of $[Al_2(OH)_2(C_{16}O_8H_6)](H_2O)_6$ (NOTT-300(Al))

$Al(NO_3)_3 \cdot 9H_2O$ (0.34 g, 0.9 mmol) was dissolved in water (10 ml), H_4L^1 (0.06 g, 0.18 mmol) was then added. Piperazine (0.1 g) was added followed by addition of 2.8 M nitric acid (2 ml). The reaction mixture was transferred to a 23 ml autoclave which was sealed and heated to 210 °C for 72 hrs. The resulting powder product was separated by filtration and washed with water to yield NOTT-300(Al) (Yield ~ 0.04 g, 53 %). Elemental analysis (% calc/found): C – 46.4/45.8, H – 1.9/2.5, N – 0.0/0.0.

5.1.2 Synthesis of $[Cr_2(OH)_2(C_{16}O_8H_6)](H_2O)_6$ (NOTT-300(Cr))

$Cr(NO_3)_3 \cdot 9H_2O$, (0.36 g, 0.9 mmol) was dissolved in water (10 mL), H_4L^1 (0.06 g, 0.18 mmol) was then added. Piperazine (0.1 g) was added followed by addition of 2.8 M nitric acid (2 mL). The reaction mixture was transferred to a 23 mL autoclave which was sealed and heated to 210 °C for 72-96 hrs. The

resulting powder product was separated by filtration and washed with water to afford NOTT-300(Cr) (Yield ~ 0.03 g, 35 %). Elemental analysis (% calc/found): C – 41.4/40.5, H – 1.7/2.0, N – 0.0/0.0.

5.1.3 Synthesis of $[\text{Al}_{1.33}\text{Cr}_{0.67}(\text{OH})_2(\text{C}_{16}\text{O}_8\text{H}_6)](\text{H}_2\text{O})_6$ (NOTT-300(AlCr2:1))

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (0.17 g, 0.72 mmol) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.07 g, 0.17 mmol) were dissolved in water (10 mL), H_4L^1 (0.06 g, 0.18 mmol) was then added. Piperazine (0.07 g) was added followed by addition of 2.8 M nitric acid (3 mL). The reaction mixture was transferred to a 23 mL autoclave which was sealed and heated to 210 °C for 72 hrs. The resulting powder product was separated by filtration and washed with water to afford NOTT-300(AlCr2:1) (Yield ~ 0.02 g, 26 %). ICP-OES – values in the range of ~ 2:1 (+/- 0.1).

5.1.4 Synthesis of $[\text{AlCr}(\text{OH})_2(\text{C}_{16}\text{O}_8\text{H}_6)](\text{H}_2\text{O})_6$ (NOTT-300(AlCr1:1))

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (0.11 g, 0.45 mmol) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.18 g, 0.45 mmol) were dissolved in water (10 mL), H_4L^1 (0.06 g, 0.18 mmol) was then added. Piperazine (0.1 g) was added followed by addition of 2.8 M nitric acid (2 mL). The reaction mixture was transferred to a 23 mL autoclave which was sealed and heated to 210 °C for 72 hrs. The resulting powder product was separated by filtration and washed with water to afford NOTT-300(AlCr1:1) (Yield ~ 0.02 g, 25 %). ICP-OES – values in the range ~1:1 (+/- 0.1).

5.1.5 Synthesis of $[\text{Al}_{0.8}\text{Cr}_{1.2}(\text{OH})_2(\text{C}_{16}\text{O}_8\text{H}_6)](\text{H}_2\text{O})_6$ (NOTT-300(AlCr2:3))

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (0.09 g, 0.72 mmol) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.21 g, 0.17 mmol) were dissolved in water (10 mL), H_4L^1 (0.06 g, 0.18 mmol) was then added.

Piperazine (0.07 g) was added followed by addition of 2.8 M nitric acid (3 mL). The reaction mixture was transferred to a 23 mL autoclave which was sealed and heated to 210 °C for 72 hrs. The resulting powder product was separated by filtration and washed with water to afford NOTT-300(AlCr₂:3) (Yield ~ 0.02 g, 25 %). ICP-OES – values in the range of ~ 2:3 (+/- 0.1).

5.1.6 Post-Synthetic Treatment of MOF Samples

There were small variations in how the samples were treated after synthesis depending on whether they were single metal or mixed metal samples. NOTT-300(Cr) and NOTT-300(Al) were washed with copious amounts of water, followed by a repeated wash with acetone. A small amount of sample (~ 5 mg) was allowed to dry in air and analysed by PXRD to confirm the desired structure. If the desired PXRD pattern was not observed, or a low quality product had been synthesised (determined by the intensity of the pattern and flatness of the baseline) the sample was discarded. AlO(OH) is sometimes a side product formed in the synthesis of NOTT-300(Al) and its presence can be detected in the PXRD pattern, if this impurity was present the sample was discarded. Samples with the correct pattern were then combined and stored in either water or acetone.

For a mixed metal sample, the same washing procedure was followed and the sample again analysed by PXRD. Like with the homometallic MOFs if the correct pattern was not observed, the sample was discarded. Once the correct structure had been determined, the metal content needed to be analysed. This was achieved by analysing each sample by ICP-OES, each sample was analysed twice to ensure repeatability in results. If the metal content (Al:Cr) was within

+/- 0.1 of the desired ratio, *i.e.* 1.1:1 for 1:1 or 2:1.1 for 2:1, the samples were combined to be used in further experiments. Samples were required to be combined as some experiments (gas sorption) require 50 - 100 mg of sample and each synthesis would yield ~ 20 mg.

All materials can be stored in acetone or water for extended periods of time (~1 year) without any apparent sample degradation.

5.2 Experimental Techniques

5.2.1 Gas Sorption

Gas sorption data were obtained by gravimetric methods using an IGA-003 system (Hiden) at the University of Nottingham. Isotherms recorded at 77 K and 87 K were measured using liquid nitrogen and liquid argon baths respectively. Isotherms recorded from 273-353 K were measured using a Grant Optima TX150 water bath. Isotherms at 368 K were measured using a cryo-furnace. All gases were ultra-pure research grade (99.999 %), except C₂H₂ which is stored in acetone, and purchased from BOC or AIRLIQUIDE. H₂ and C₂H₂ were further purified before use by using calcium aluminosilicate and activated carbon adsorbents to remove trace amounts of impurities, such as water (H₂) or acetone (C₂H₂) which could affect the adsorption data. In a typical gas sorption experiment 50 – 100 mg of sample was loaded onto the IGA and degassed at 393 K under high vacuum (10⁻⁷ bar) for 1 day to give fully desolvated material. For flow experiments the flow rates for each gas were controlled by two identical mass flow controllers.

Breakthrough experiments were carried out in a fixed bed tube, 7 mm in diameter and 130 mm in length, packed with ~3 g of NOTT-300(Al) powder. The total bed volume was 5 cm³. Before the experiments were recorded the sample was heated to 100 °C under a constant flow of He for ~12 hours to ensure complete activation. The breakthrough experiments were performed at 293 K, and the temperature was controlled by a Grant Optima TX150 water bath. The composition of the exiting gas stream was determined by mass spectroscopy.

The dimensionless time (τ) was obtained by dividing the actual time recorded (t) by the contact time between the gas and the sample ($\epsilon L/u$).

$$\tau = \frac{tu}{\epsilon L} \quad (5.1)$$

The following parameters are used for the calculation - bed diameter, d , (7 mm) bed length, L , (120 mm), flow rate (2 ml min⁻¹), bed volume, (5 ml), sample mass (3.4 g) and sample framework density (1.06 g cc⁻¹). The total volume occupied by the sample is 3.21 ml therefore the fractional porosity, ϵ , of the fixed bed is 0.358. The superficial gas velocity, u , corresponds to 8.66 e⁻⁴ m s⁻¹. Therefore the contact time between the gas and the NOTT-300(Al) sample is calculated to be 49.61 s.

5.2.2 Synchrotron X-ray Powder Diffraction and Structure Determination

High resolution *in situ* synchrotron X-ray powder diffraction (PXRD) data were collected at Beamline I11 of Diamond Light Source using multi-analysing crystal-detectors (MACs) and monochromated radiation. The diffraction measurements were carried out in capillary mode and the temperature controlled by an Oxford Cryosystems nitrogen gas cryostat. Before the experiment, the

powder sample of NOTT-300 was dried in air and ground thoroughly before loading into a capillary tube (0.7 mm diameter). Grinding provides a uniform particle size essential for obtaining high quality X-ray patterns. The capillary tube was connected to a high vacuum line (10^{-6} mbar) and heated at 140 °C for ~2 hours to generate the fully desolvated NOTT-300 material. The gas was loaded into the sample at room temperature to ensure sufficient mobility of the gas inside the framework and allowed time to equilibrate (~ 1 hour). The equilibration process was monitored by short PXRD scans, and once the pattern had ceased changing equilibrium was assumed and the PXRD pattern was recorded. The gas flow was controlled by a fully automated gas panel that allows for precise dosing of certain pressures.

The structure refinement of all NOTT-300(Cr) and AlCr(2:1) samples (activated and gas loaded) were carried out by Chris Morris and the structural refinement of the NOTT-300(Al) samples was carried out by Dr. Sihai Yang and Dr. Anibal (Timmy) Ramirez-Cuesta. The activated frameworks were refined using the published NOTT-300(Al) structure. For each of the gas-loaded structures, the activated structure was added to the model along with two rigid bodies of gas. The orientation and position of these rigid bodies were refined, followed by a refinement of the soft-restrained framework.

Owing to the location of the main adsorption site in the framework the gas molecules exhibit positional disorder, site(I) can be located either side of the -OH group. For clarity this disorder is omitted from structural figures.

5.2.3 Inelastic Neutron Scattering

INS spectra were recorded on the TOSCA instrument at the ISIS Facility at the Rutherford Appleton Laboratory for energy transfers between -2 and 500 meV.

The NOTT-300(Al) sample was loaded into a cylindrical vanadium sample container with an indium vacuum seal and prior to data collection was degassed at 120 °C and 10^{-7} mbar for 1-2 days to ensure full removal of water from the pores. The sample cell was connected to a manual gas panel that allowed for controlled dosing of up to 1 bar of gas. The temperature during data collection was controlled with a closed cycle refrigerator (CCR) cryostat. Gas loading was performed at room temperature to ensure the C₂ hydrocarbons were present in the gas phase and to ensure sufficient mobility of the gas molecules within the framework host. The sample was then cooled to ~ 11 K to ensure minimum achievable thermal motion of the framework host and adsorbed gas molecules. The difference spectra were obtained by subtracting the background spectrum from the gas loaded spectra. Solid C₂H₂, C₂H₄ and C₂H₆ spectra were measured by using a plate sample container and each gas was condensed slowly and cooled to ~ 10 K for the measurement.

5.2.4 Physical Characterisation

Thermogravimetric analysis was carried out under a flow of Nitrogen (5 mL min⁻¹) on a Perkin-Elmer Pyris1 Thermogravimetric analyser. The scan was recorded up to 1000 °C with a heating rate of 5 °C min⁻¹. At least 10 mg of sample was used to minimise the error associated with the mass loss.

Elemental analysis for C, H and N content of complexes were carried out using a CE-440 Elemental Analyzer manufactured by Exeter Analytical.

ATR-FTIR spectra were recorded on a Nicolet i5 FT-IR spectrophotometer with a diamond ATR attachment in a sealed glove bag. The glove bag was purged with N₂ at least 3 times to ensure a N₂ environment inside the instrument and the

glove bag. The gas loaded *in situ* IR studies were carried out by Dr Timothy Easun at Diamond Light Source using an environmentally controlled cell.

ICP-OES measurements were carried out using a Perkin-Elmer Optima 2000. Prior to ICP-OES measurements, a 3-5 mg sample of mixed metal MOF was digested in Aristar grade nitric acid (69 %) for 12 hrs with heating to ensure all metals are digested. The sample was then filtered using a syringe filter to remove any residual ligand and diluted with ultra-pure water to the required concentration for analysis.

5.2.5 Heat of adsorption calculations

The heats of adsorption and entropies for the gas sorption experiments carried out in this thesis were calculated using the van't Hoff isochore. The isotherms recorded at 273 – 303 K (or higher, if the data is available) were fitted to the following equation (van't Hoff).

$$\ln(p) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (5.2)$$

Where p is the pressure in Pa, T is the temperature and R is the real gas constant. A plot of $\ln(p)$ vs. $1/T$ allows the enthalpy and entropy of adsorption to be determined. Examples of linear fitting plots are shown in Appendix 3.

Chapter 6 - Conclusion

The aim of this thesis was to synthesise a novel MOF analogous to NOTT-300(Al) in order to investigate how the change in metal centre will affect the gas adsorption properties of the material. This idea was further expanded by the synthesis of a series of novel heterometallic MOFs containing varying ratios of Al and Cr to see if not just the metal centre but the ratios of each metal present could affect the gas adsorption properties of the materials. If a particular trend exists within these mixed metal materials this could provide potentially useful information predictive design, particularly in terms of fine tuning microporous materials for a specific function.

Chapter 2 discusses the synthesis and structure of the novel material NOTT-300(Cr) and its structural similarities and differences to NOTT-300(Al). The framework consists of the same overall structure, with the metal-bridging -OH groups protruding into the pores and available for interaction with guest species. Due to the difference in size/electronics between Al(III) and Cr(III) there are slight structural changes in NOTT-300(Cr), such as an expansion in unit cell, slightly larger pore diameter and longer Cr-O bonds. These slight differences are all expected to contribute to differences in gas adsorption. Other properties are also affected by a change in metal centre, such as thermal stability; NOTT-300(Cr) has a higher thermal decomposition temperature than NOTT-300(Al) by ~ 50 °C. The main focus of Chapter 2 was to investigate how these small changes in structure affect the CO₂ adsorption capacity and selectivity and to do this, several CO₂ adsorption isotherms were recorded. Additionally, other gas (CH₄, CO, N₂) adsorption isotherms were recorded and the interactions between CO₂ and the framework were investigated by *in situ* PXRD studies. NOTT-300(Cr) displays a high affinity for CO₂,

reaching a maximum uptake of $10.95 \text{ mmol g}^{-1}$ at 195 K and 1 bar. This high adsorption is maintained on increase in temperature to 273 K, with the uptake reaching $10.08 \text{ mmol g}^{-1}$. Both of these uptakes are higher than those reached by NOTT-300(Al). In fact, at 195 K NOTT-300(Al) has a much lower uptake, reaching only 2.95 mmol g^{-1} , which we propose may be due to the narrower pores in NOTT-300(Al) restricting the diffusion of the CO_2 , and this additional diffusion barrier not being overcome at such low temperatures. These initial results show how the change in metal centre can, through small cumulative effects, have a large effect on the gas adsorption properties in this series of frameworks. At low pressures ($< 0.15 \text{ bar}$), it can be seen that the CO_2 isotherm for NOTT-300(Al) is steeper than that of NOTT-300(Cr), indicating a stronger interaction between the framework and the CO_2 molecules. This was confirmed by the CO_2 loaded PXRD studies that were carried out, which found that the H-bond between the CO_2 and the -OH group was longer in NOTT-300(Cr) than in NOTT-300(Al) by $0.2 \text{ \AA}$. However, it was also found that the dipole interaction between the adsorbed CO_2 molecules was stronger in NOTT-300(Cr) and the interaction between the CO_2 and the -OH group in NOTT-300(Cr) was still sufficiently strong to afford this material a high CO_2 selectivity ($\text{CO}_2/\text{N}_2 - 84$, $\text{CO}_2/\text{CH}_4 - 15$). These stronger dipole interactions and slight increase in space and pore diameter are what gives NOTT-300(Cr) increased adsorption capacity at higher pressures when the interactions between the adsorbed species plays the more dominant role in further facilitating adsorption. The calculated heat of adsorption at zero loading for CO_2 in NOTT-300(Cr) was lower than that reported for NOTT-300(Al), which also correlates well with the results found by PXRD, and suggests the increased total uptake in NOTT-300(Cr) could be due

to kinetics/space. This was further supported by the gas loaded IR studies that were carried out, that clearly show the CO₂ interacts more strongly with the framework when Al is the metal centre present. This is shown by the large change in wavenumber of the $\nu(\text{OH})$ peak when CO₂ is introduced into the environment, with the same experiment conducted on NOTT-300(Cr) showing a much smaller shift which we ascribed to a weaker interaction.

Although these changes have positive effects on the CO₂ adsorption capacity, NOTT-300(Cr) also has a higher adsorption capacity for other gases (CH₄, CO *etc.*) than NOTT-300(Al) and therefore has a lower CO₂ selectivity. Clearly there is a problem – trying to increase adsorption capacity whilst maintaining the high selectivity is not straightforward.

Further gas adsorption experiments (breakthrough) were conducted on NOTT-300(Al) in order to assess the separation capability in real time and the material successfully separated CO₂/N₂ streams to a high purity.

To further this work, the same breakthrough experiments could be conducted on NOTT-300(Cr) to see how the differences in kinetics affects the separation capabilities. The differences in the thermodynamics have been probed already in this work by gas loaded PXRD and IR. The gas loaded IR was able to indicate that the kinetics of CO₂ release in NOTT-300(Al) were slower than NOTT-300(Cr), which may be beneficial in breakthrough experiments, however, again there is a trade-off as a separation material that takes a long time is not very efficient.

In Chapter 3 the synthesis of three novel mixed metal materials with the NOTT-300 structure containing differing ratios of Al and Cr is achieved and

discussed. The materials successfully synthesised are NOTT-300(AlCr2:1), NOTT-300(AlCr1:1) and NOTT-300(AlCr2:3) and the CO₂ adsorption properties were studied and probed for a trend amongst the series. The presence of a third bridging -OH group was confirmed by IR in all materials, thus proving the materials are heterometallic MOFs and not a mix of separate NOTT-300(Al) and NOTT-300(Cr). Each of the mixed metal materials displays quite a different gas adsorption profile and there does not appear to be an overall trend based on metal content. For example, not only do the three materials have different N₂ adsorption capacities but the shapes of the isotherms are also different. Each of the heterometallic MOFs displayed different CO₂ adsorption capacities that were not merely a summative combination of appropriate proportions of the NOTT-300(Al) and NOTT-300(Cr) properties. Each of the materials display a high CO₂ adsorption capacity with AlCr2:1 reaching the highest uptake, 9.87 mmol g⁻¹ (AlCr2:1), 9.50 mmol g⁻¹ (AlCr1:1) and 8.57 mmol g⁻¹ (AlCr2:3). AlCr2:1 also has the highest heat of adsorption for CO₂ of the mixed metal series, indicating stronger interactions between the CO₂ and the framework. The fact that AlCr2:1 displays the highest CO₂ adsorption capacity, even though it has the highest Al content and NOTT-300(Al) has a lower uptake than NOTT-300(Cr), clearly shows that there is more to this than metal content. Some of these differences can be attributed to the presence of the new Al-OH-Cr moiety which was shown to be present by IR. The CO₂ selectivity also varies across the series, with no specific trend to be seen.

A combination of CO₂ loaded PXRD and IR studies were used to probe how this new -OH group interacts with the CO₂ molecules. The PXRD data showed that although the CO₂-OH interactions were weaker than in both NOTT-300(Al) and

NOTT-300(Cr), as shown by a longer H-bond distance, the CO₂-CO₂ interactions are stronger in AlCr₂:1 than they are in NOTT-300(Al). It is not possible *via* PXRD to investigate the interaction between CO₂ and each different -OH group. The combination of PXRD and IR allowed us to characterise the “overall” interaction with the framework, as well as to monitor how each -OH group shifts with respect to CO₂ concentration. This also gives an idea into the strength of the interaction. The IR spectra clearly show that both Al-OH-Al and Al-OH-Cr interact more strongly than Cr-OH-Cr with the adsorbed CO₂ molecules. This is displayed by the large shift in wavenumber for the $\nu(\text{OH})$ peak for Al-OH-Cr than for Cr-OH-Cr, which doesn't shift at all but merely broadens. The shift for Al-OH-Cr is comparable to Al-OH-Al and previously PXRD data has shown that the H-bonds between the -OH group and the CO₂ are stronger in NOTT-300(Al) than NOTT-300(Cr). However, the PXRD for AlCr₂:1 gives an average of the three (or more) different interactions (Al-OH-Al, Cr-OH-Cr and Al-OH-Cr), therefore it is reasonable to assume that the interactions between Al-OH-Cr and CO₂ are similar in strength to those found in NOTT-300(Al).

Chapter 3 clearly shows that each heterometallic MOF has its own CO₂ adsorption profile and selectivity, however, there is no apparent trend with respect to cation content. It has been shown that the presence of the Al-OH-Cr moiety interacts differently with the CO₂ than Al-Al and Cr-Cr and therefore the amount of Al-Cr in the MOF will have effects on the CO₂ adsorption. One avenue to take this study on would be to investigate the distribution of the metals within the samples of the different ratios, and also of the same ratios to investigate how much variation there is between samples and if the metal

distribution has a large effect on the gas adsorption properties. The spatial distribution of the metals is expected to have an effect as each of the three -OH groups have different strength interactions with the CO₂. This could prove interesting as IR suggests there are truly mixed metal sites in the MOF but gives no information on the distribution of these sites and this could be pursued by analysing samples by EDX and other mapping techniques. Another analysis that could be performed that could provide an insight to the difference in gas adsorption properties would be to measure the pK_a of the -OH group; a drawback to this method is that it requires a large amount of sample and it is unclear without further study if the technique would be able to distinguish between the different -OH groups within the mixed metal samples.

Chapter 4 uses the previously discussed MOFs and assesses the C₂ hydrocarbon adsorption properties again probing for a trend amongst the properties with respect to the metal centre and also the amount of each metal centre. There are two ways in which MOFs exhibit C₂ selectivity: through size selective adsorption, and through differences in interaction strength, however, with literature examples each of these methods have limitations. The NOTT-300 series appears to be able to separate C₂ hydrocarbons *via* both processes without the current drawbacks. As the experiments with NOTT-300(Al) have shown that a combination of narrow pore windows and a site available for interaction leads to a high CO₂ selectivity without limited uptake or water instability. All materials displayed a higher adsorption affinity for C₂H₂ than C₂H₄, C₂H₆ and CH₄ with NOTT-300(Cr) and AlCr₂:1 displaying the highest adsorption of 7.33 mmol g⁻¹ and 7.53 mmol g⁻¹ respectively. The following materials displayed the following favourable selectivities: NOTT-300(Al) – C₂H₂/C₂H₄ (4.3), C₂H₂/C₂H₆ (28.2),

$\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ (3.1), $\text{AlCr2:1} - \text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (2.9), $\text{C}_2\text{H}_2/\text{C}_2\text{H}_6$ (3.2), $\text{AlCr1:1} - \text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (2.4), $\text{C}_2\text{H}_2/\text{C}_2\text{H}_6$ (7.8), $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ (2.7) and $\text{AlCr2:3} - \text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (2.6), $\text{C}_2\text{H}_2/\text{C}_2\text{H}_6$ (7.8), $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ (2.5), $\text{NOTT-300(Cr)} - \text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (2.4), $\text{C}_2\text{H}_2/\text{C}_2\text{H}_6$ (2.8). Each of the materials displays high C_2/CH_4 selectivity owing to the differences in interaction strength and NOTT-300(Al) displays the highest C_2 selectivities across the series, thought to be due to the combination of narrower pores and the strong interactions formed with the framework. As each of the mixed metal materials displayed quite different C_2 adsorption profiles, with both AlCr1:1 and AlCr2:3 having increased adsorption of C_2H_6 with increase in temperature for example, there is no apparent trend in adsorption or selectivity with respect to metal content. However, due to these differences in adsorption at different temperatures, the selectivity varies across the series so it is possible to select a particular sample that performs more efficiently at a given temperature. For example, for $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ separations at 273 K AlCr2:1 performs best, whereas at 303 K AlCr2:3 has a higher selectivity. Although a trend would have been advantageous for further study in terms of predictive design for increasing adsorption/selectivity, this is still a promising result. To take this further, again structural mapping would be beneficial, to investigate how the distribution of metal centres effects the C_2 hydrocarbon adsorption and see if that is maybe behind the increased adsorption of some gases at higher temperatures. Another key, yet surprising result, came from the $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ separation performed through breakthrough experiments on NOTT-300(Al) . All analysis previously performed (PXRD, INS) and the single and dual component adsorption isotherms suggested that NOTT-300(Al) had preferential adsorption for C_2H_4 due to stronger interactions, as shown by the shorter H-bonds formed

by C_2H_4 . However, the separation of a C_2H_4/C_2H_6 gas stream was achieved by the sample retaining C_2H_6 and eluting C_2H_4 first, to a purity level $> 99\%$. This was likely due to the slow diffusion of C_2H_6 along the pores; the C_2H_4 can travel faster as not only is it smaller in size but it interacts with $-OH$, possibly helping it shuttle along and making it able to pass through the sample quicker than C_2H_6 (elution time – $C_2H_6 \sim 45$ mins, $C_2H_4 \sim 10$ mins).

Through a combination of different spectroscopic analyses, gas adsorption experiments and selectivity calculations we were able to thoroughly probe the selectivity (CO_2 and C_2) of the NOTT-300(Al/Cr) series. These experimental (dual component gas adsorption experiments and breakthrough experiments) and theoretical (IAST) techniques worked well together for probing the selectivity of these materials. The gas loaded studies (PXRD, IR and INS) provided valuable insights into the interactions formed between the adsorbed species, allowing the difference in gas uptake/selectivity to be explained. There are many ways in which this work can be furthered. For instance, there are some experiments that have only been performed on NOTT-300(Al), such as neutron spectroscopy and breakthrough experiments, that could also be carried out on the rest of the series. Also, a further study on how the gases travel along the pores could provide some useful and interesting information into the kinetics of the adsorbed species in these frameworks. Also, as mentioned previously, further investigation into the structural mapping of and differences in said mapping of the mixed metal series could provide some key insights to the differences in the gas adsorption.

Appendices

Appendix 1 – Crystal Data – Atomic Positions

Desolvated NOTT-300(Cr)

	$a=b$ (Å)	c (Å)	V (Å ³)
Unit cell	14.9905(2)	11.9905(1)	2694.44(1)

	x	y	z	$Occ.$	B_{iso}
Cr	0.69052(3)	0.30948(3)	0.50000	1	1.342(13)
O1	0.74908(14)	0.25000	0.62500	1	1.986(25)
O2	0.89797(9)	0.28801(9)	0.99619(13)	1	1.986(25)
O3	0.62018(11)	0.37997(11)	0.39391(12)	1	1.986(25)
C1	0.59564(17)	0.36098(15)	0.70147(19)	1	1.435(30)
C2	0.54232(14)	0.43186(14)	0.75887(23)	1	1.435(30)
C3	0.50000	0.50000	0.70116(22)	1	1.435(30)
C4	0.54756(17)	0.43329(16)	0.87781(15)	1	1.435(30)
C5	0.50000	0.50000	0.93608(19)	1	1.435(30)
H3	0.50000	0.50000	0.6236(17)	1	1.722(36)
H4	0.57318	0.38162	0.90735	1	1.722(36)
H1	0.80600	0.25000	0.62500	1	1.722(36)

CO₂ Loaded NOTT-300(Cr)

	$a=b$ (Å)	c (Å)	V (Å ³)
Unit cell	14.9947(2)	11.9865(2)	2695.07(1)

	x	y	z	$Occ.$	B_{iso}
Cr	0.69100(4)	0.30900(4)	0.50000	1	1.222(28)
O1	0.75310(16)	0.25000	0.62500	1	0.952(38)
O2	0.89928(11)	0.28562(11)	0.99428(16)	1	0.952(38)
O3	0.62151(13)	0.37955(14)	0.39148(13)	1	0.952(38)
C1	0.58896(19)	0.35757(21)	0.70010(23)	1	0.663(53)
C2	0.54290(19)	0.43220(18)	0.75885(27)	1	0.663(53)
C3	0.50000	0.50000	0.70170(29)	1	0.663(53)
C4	0.54794(20)	0.43341(21)	0.87804(20)	1	0.663(53)
C5	0.50000	0.50000	0.93610(22)	1	0.663(53)
H3	0.50000	0.50000	0.6241(20)	1	0.796(63)
H4	0.57318	0.38162	0.90735	1	0.796(63)
H1	0.80600	0.25000	0.62500	1	0.796(63)
C6	-0.24097	-0.04477	0.30931	0.500(26)	28.24(47)

O4	-0.22873(5)	-0.12243(31)	0.30809(0)	0.500(26)	28.24(47)
O5	-0.25321(5)	0.03289(31)	0.31053(0)	0.500(26)	28.24(47)
C7	0.20719(21)	0.10296(24)	0.06901(69)	0.500(19)	28.61(33)
O6	0.23619(46)	0.11092(48)	0.15636(94)	0.500(19)	28.61(33)
O7	0.17819(46)	0.09500(48)	-0.01834(94)	0.500(19)	28.61(33)

C₂H₂ Loaded NOTT-300(Cr)

	<i>a</i> = <i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
Unit cell	14.9892(3)	11.9816(3)	2691.79(2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>Occ.</i>	<i>B</i> _{iso}
Cr	0.69029(5)	0.30971(5)	0.50000	1	2.219(35)
O1	0.76238	0.25000	0.62500	1	1.836(61)
O2	0.90314	0.29264	1.00000	1	1.836(61)
O3	0.61740	0.37559	0.39379	1	1.836(61)
C1	0.59248	0.36173	0.69421	1	3.446(86)
C2	0.54690	0.43365	0.75937	1	3.446(86)
C3	0.50000	0.50000	0.69946	1	3.446(86)
C4	0.54518	0.43216	0.87780	1	3.446(86)
C5	0.50000	0.50000	0.93608	1	3.446(86)
H3	0.50000	0.50000	0.62411	1	4.13(10)
H4	0.57318	0.38162	0.90735	1	4.13(10)
H1	0.80600	0.25000	0.62500	1	4.13(10)
C6	0.1371(19)	0.3274(14)	1.2878(21)	0.500(37)	20.1(10)
C7	0.1722(37)	0.2581(25)	1.3148(40)	0.500(37)	20.1(10)
C10	0.2422(13)	0.05578(95)	-0.5255(14)	0.500(34)	9.42(46)
C11	0.250(27)	0.048(27)	-0.623(26)	0.500(34)	9.42(46)

Desolvated AlCr₂:1

	<i>a</i> = <i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
Unit cell	14.8654(2)	11.8655(3)	2622.03(10)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>Occ.</i>	<i>B</i> _{iso}
Al/Cr	0.69356(20)	0.30744(20)	0.50000	1	0.10(19)
O1	0.74241(12)	0.25000	0.62500	1	0.10(16)
O2	0.89270	0.28393	0.99415	1	0.10(16)
O3	0.62519	0.37263	0.39375	1	0.10(16)

C1	0.59212	0.35796	0.70592	1	0.1(3)
C2	0.54079	0.42965	0.75859	1	0.1(3)
C3	0.50000	0.50000	0.70365	1	0.1(3)
C4	0.54303	0.43111	0.87836	1	0.1(3)
C5	0.50000	0.50000	0.93683	1	0.1(3)
H3	0.50000	0.50000	0.62529	1	0.1(4)
H4	0.57318	0.38162	0.90735	1	0.1(4)
H1	0.80600	0.25000	0.62500	1	0.1(4)

CO₂ Loaded AlCr 2:1

	$a=b$ (Å)	c (Å)	V (Å ³)
Unit cell	14.8731(2)	11.8512(2)	2621.59(9)

	x	y	z	$Occ.$	B_{iso}
Al/Cr	0.69312(24)	0.30688(24)	0.50000	1	1.3(2)
O1	0.74944(72)	0.25000	0.62500	1	0.4(2)
O2	0.89865(50)	0.28489(54)	0.9951(11)	1	0.4(2)
O3	0.62284(64)	0.37567(61)	0.39577(63)	1	0.4(2)
C1	0.5923(12)	0.3564(13)	0.6951(15)	1	0.4(3)
C2	0.54137(90)	0.43005(94)	0.7563(14)	1	0.4(3)
C3	0.50000	0.50000	0.7003(16)	1	0.4(3)
C4	0.54406(93)	0.43115(91)	0.87665(89)	1	0.4(3)
C5	0.50000	0.50000	0.9359(13)	1	0.4(3)
H3	0.50000	0.50000	0.622(11)	1	0.5(4)
H4	0.57318	0.38162	0.90735	1	0.5(4)
H1	0.80600	0.25000	0.62500	1	0.5(4)
C6	0.2342(15)	0.0484(13)	0.3068(17)	0.490(18)	21(2)
O4	0.2124(24)	0.1232(22)	0.2937(46)	0.490(18)	21(2)
O5	0.2560(24)	-0.0265(22)	0.3200(46)	0.490(18)	21(2)
C7	0.2085(12)	0.1035(15)	0.0537(35)	0.500(13)	20(2)
O6	0.1735(28)	0.1006(27)	-0.0328(45)	0.500(13)	20(2)
O7	0.2434(28)	0.1065(27)	0.1402(45)	0.500(13)	20(2)

Desolvated NOTT-300(Al)

	$a=b$ (Å)	c (Å)	V (Å ³)
Unit cell	14.8296(1)	11.7732(1)	2589.11(3)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>Occ.</i>	<i>B_{iso}</i>
Al	0.69426(5)	0.30574(5)	0.50000	1	0.72(13)
O1	0.75744(13)	0.25000	0.62500	1	0.51(12)
O2	0.89782(9)	0.28675(9)	0.99869(15)	1	0.51(12)
O3	0.62165(10)	0.37371(10)	0.39436(12)	1	0.51(12)
C1	0.59280(15)	0.36039(14)	0.69453(19)	1	0.70(13)
C2	0.54498(10)	0.43181(7)	0.75722(10)	1	0.70(13)
C3	0.50000	0.50000	0.69649(14)	1	0.70(13)
C4	0.54071(10)	0.428618(71)	0.87716(8)	1	0.70(13)
C5	0.50000	0.50000	0.93474(11)	1	0.70(13)

C₂H₂ Loaded NOTT-300(Al)

	<i>a=b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
Unit cell	14.8228(1)	11.7919(1)	2590.86(5)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>Occ.</i>	<i>B_{iso}</i>
Al	0.69415(8)	0.30585(8)	0.50000	1	0.63(12)
O1	0.75552(18)	0.25000	0.62500	1	0.30(12)
O2	0.89613(13)	0.28645(13)	0.99610(19)	1	0.30(12)
O3	0.62081(14)	0.37512(14)	0.39396(15)	1	0.30(12)
C1	0.58992(23)	0.35603(21)	0.69874(25)	1	0.30(12)
C2	0.58992(23)	0.35603(21)	0.76206(15)	1	0.30(12)
C3	0.50000	0.50000	0.70562(15)	1	0.30(12)
C4	0.53767(12)	0.42905(1)	0.88125(15)	1	0.30(12)
C5	0.50000	0.50000	0.93719(17)	1	0.30(12)
H3	0.50000	0.50000	0.6290	1	0.36(14)
H4	0.57318	0.38162	0.90735	1	0.36(14)
H1	0.81486	0.25000	0.62500	1	0.36(14)
C6a	0.04267	0.25000	0.67013	0.500(20)	5.65(27)
H6a	0.04267	0.25000	0.75689	0.500(20)	5.65(27)
C6b	0.04281	0.25000	0.56998	0.500(20)	5.65(27)
H6b	0.04281	0.25000	0.48323	0.500(20)	5.65(27)
C7a	0.12722	0.34688	0.26520	0.500(23)	6.88(36)
H7a	0.10815	0.41009	0.23993	0.500(23)	6.88(36)
C7b	0.14929	0.27397	0.29453	0.500(23)	6.88(36)
H7b	0.16836	0.21076	0.31980	0.500(23)	6.88(36)

C₂H₄ Loaded NOTT-300(Al)

	$a=b$ (Å)	c (Å)	V (Å ³)
Unit cell	14.8047(2)	11.8017(1)	2586.69(1)

	x	y	z	$Occ.$	B_{iso}
Al	0.69415(5)	0.30585(5)	0.50000	1	0.940(24)
O1	0.75401(12)	0.25000	0.62500	1	0.498(20)
O2	0.62233(28)	0.37947(30)	0.60369(21)	1	0.498(20)
O3	0.60473(30)	0.28484(20)	0.74714(25)	1	0.498(20)
C1	0.59305(22)	0.35991(18)	0.70027(18)	1	0.988(28)
C2	0.54174(8)	0.42942(6)	0.76252(15)	1	0.988(28)
C3	0.50000	0.50000	0.70313(18)	1	0.988(28)
C4	0.54174(8)	0.42942(6)	0.88130(11)	1	0.988(28)
C5	0.50000	0.50000	0.94069(10)	1	0.988(28)
H3	0.50000	0.50000	0.61416	1	1.186(33)
H4	0.57301	0.37655	0.92578	1	1.186(33)
H1	0.81480	0.25000	0.62500	1	0.597(24)
C6a	0.55036	0.75000	0.13829	0.3531(24)	16.58(57)
H6a	0.51077	0.70046	0.09187	0.3531(24)	16.58(57)
H6b	0.59292	0.79754	0.09271	0.3531(24)	16.58(57)
C6b	0.54676	0.75245	0.24661	0.3531(24)	16.58(57)
H6c	0.58618	0.80213	0.29302	0.3531(24)	16.58(57)
H6d	0.50412	0.70498	0.29218	0.3531(24)	16.58(57)
C7a	0.15000	0.32200	0.19600	0.2805(22)	20.00(93)
H7a	0.12250	0.3739	0.2509	0.2805(22)	24.0(11)
H7b	0.177	0.3400	0.113	0.2805(22)	24.0(11)
C7b	0.152	0.2397	0.229	0.2805(22)	20.00(93)
H7c	0.180	0.1878	0.174	0.2805(22)	24.0(11)
H7d	0.126	0.2217	0.312	0.2805(22)	24.0(11)

C₂H₆ Loaded NOTT-300(Al)

	$a=b$ (Å)	c (Å)	V (Å ³)
Unit cell	14.7955(1)	11.7785(2)	2578.38(6)

	x	y	z	$Occ.$	B_{iso}
Al	0.6924(5)	0.3076(5)	0.50000	1	0.50(29)
O1	0.7520(4)	0.25000	0.62500	1	2.22(11)
O2	0.6213(6)	0.3803(6)	0.6009(5)	1	2.22(11)

O3	0.6039(6)	0.2876(4)	0.7426(6)	1	2.22(11)
C1	0.5927(4)	0.3614(4)	0.6963(4)	1	0.926(73)
C2	0.5428(2)	0.4304(1)	0.7579(3)	1	0.926(73)
C3	0.50000	0.50000	0.6987(4)	1	0.926(73)
C4	0.5428(2)	0.4304(1)	0.8763(2)	1	0.926(73)
C5	0.50000	0.50000	0.9356(2)	1	0.926(73)
H3	0.50000	0.50000	0.6121	1	0.926(73)
H4	0.5740	0.3796	0.3796	1	0.926(73)
H1	0.8128	0.25000	0.6250	1	2.22(11)
C6a	0.0091	0.2232	0.6264	0.2178(17)	3.00(30)
H6a	0.0032	0.1504	0.6118	0.2178(17)	3.00(30)
H6b	-0.0508	0.2568	0.5922	0.2178(17)	3.00(30)
H6c	0.0134	0.2368	0.7175	0.2178(17)	3.00(30)
C6b	0.0942	0.2583	0.5665	0.2178(17)	3.00(30)
H6d	0.0997	0.3311	0.5804	0.2178(17)	3.00(30)
H6e	0.0889	0.2441	0.4757	0.2178(17)	3.00(30)
H6f	0.1534	0.2240	0.6017	0.2178(17)	3.00(30)
C7a	0.1366	0.2972	0.2623	0.1294(16)	2.04(50)
H7a	0.0913	0.2954	0.3355	0.1294(16)	2.04(50)
H7b	0.2038	0.2750	0.2888	0.1294(16)	2.04(50)
H7c	0.1117	0.2519	0.1960	0.1294(16)	2.04(50)
C7b	0.1412	0.3944	0.2170	0.1294(16)	2.04(50)
H7d	0.1871	0.3964	0.1443	0.1294(16)	2.04(50)
H7e	0.1662	0.4388	0.2842	0.1294(16)	2.04(50)
H7f	0.0736	0.4156	0.1909	0.1294(16)	2.04(50)

Appendix 2: Fitting of the Adsorption Isotherms Using a Langmuir Model

The single component adsorption isotherms for CO₂, CH₄, N₂, CO, O₂, C₂H₂, C₂H₄ and C₂H₆ in NOTT-300(Cr), AlCr₂:1, AlCr₁:1 and AlCr₂:3 at 273 - 303 K were fitted using a single site Langmuir model.

$$n = \frac{q_{sat} b P^v}{1 + b P^v}$$

Where n is the amount adsorbed in mmol g⁻¹, q_{sat} is the saturation capacity in mmol g⁻¹, b is the Langmuir parameter in bar⁻¹, P is the pressure in bar and v is the Freundlich parameter. The fitting of the CO₂ adsorption isotherm in NOTT-300(Cr) at 273 K and 293 K is shown as an example in Fig(A1) and all the fitted parameters are listed below.

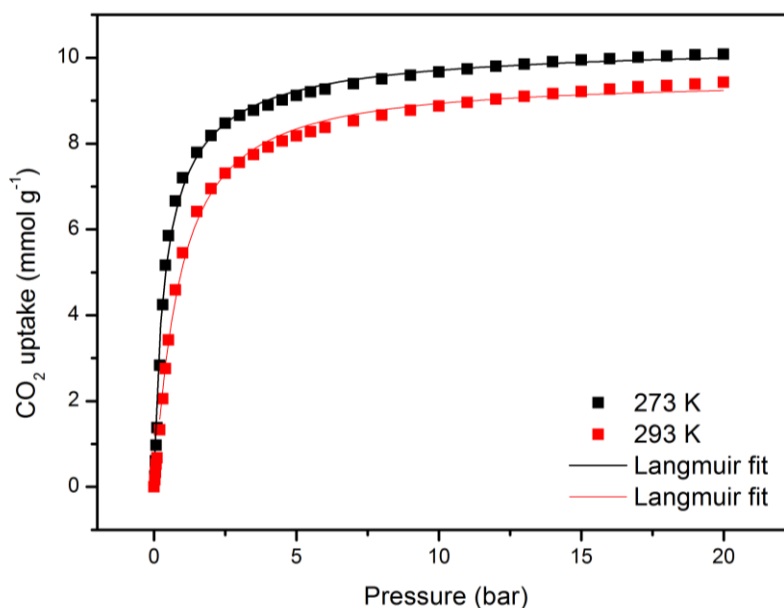


Fig. A1 – Adsorption of CO₂ in NOTT-300(Cr) at 273 K and 293 K from 0 – 20 bar with Langmuir fits shown.

A2.1 CO₂

NOTT-300(Cr)	q _{sat}	Standard error	b	Standard error	v	Standard error	Adj. R ²
273 K	10.38302	0.04157	2.03434	0.04223	0.84865	0.01942	0.9949
283 K	9.78475	0.07296	1.65479	0.06924	1.08872	0.03335	0.9974
293 K	9.51252	0.06711	1.18673	0.03755	1.11426	0.02876	0.9982
303 K	9.45019	0.03959	0.82501	0.01138	1.04348	0.01808	0.9965

AlCr2:1	q _{sat}	Standard error	b	Standard error	v	Standard error	Adj. R ²
273 K	9.70087	0.08544	3.08384	0.2506	1.1803	0.05936	0.9959
283 K	9.58243	0.06244	1.94358	0.08089	1.1057	0.03217	0.9969
293 K	9.40047	0.05797	1.30519	0.03797	1.11218	0.02631	0.9983
303 K	9.17498	0.04846	0.88515	0.01719	1.13522	0.01988	0.9991

AlCr1:1	q _{sat}	Standard error	b	Standard error	v	Standard error	Adj. R ²
273 K	9.3392	0.08437	3.03477	0.22964	1.07335	0.0511	0.9999
283 K	9.12813	0.08133	1.98276	0.11061	1.09399	0.04545	0.9999
293 K	9.0646	0.08848	1.26231	0.05556	1.0681	0.03976	0.9998
303 K	8.99494	0.07609	0.84559	0.02448	1.07984	0.02864	0.9999

AlCr2:3	q _{sat}	Standard error	b	Standard error	v	Standard error	Adj. R ²
273 K	8.51538	0.08209	2.61938	0.17717	1.00139	0.04391	0.9998
283 K	8.56945	0.08453	1.87197	0.10756	1.03881	0.04273	0.9999
293 K	8.62677	0.08822	1.22443	0.05554	1.04071	0.03639	0.9997
303 K	8.68535	0.08469	0.79638	0.02562	1.0356	0.02714	0.9997

A2.2 CH₄

NOTT-300(Cr)	q _{sat}	Standard error	b	Standard error	v	Standard error	Adj. R ²
273 K	7.75664	0.02974	0.25895	0.00256	1.2714	0.01038	0.9998
283 K	8.0817	0.05258	0.17526	0.00204	1.16999	0.01145	0.9998
293 K	7.73509	0.04144	0.14479	0.00135	1.19554	0.00912	0.9999
303 K	7.96188	0.06264	0.15055	0.00155	1.06276	0.00942	0.9998

AlCr2:1	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	7.79939	0.13438	0.13676	0.004	1.19654	0.02853	0.9991
283 K	8.39325	0.13912	0.10316	0.00234	1.17559	0.02206	0.9995
293 K	7.73616	0.09694	0.14107	0.00282	1.16577	0.0194	0.9995
303 K	8.82449	0.11696	0.12522	0.00176	0.995	0.01151	0.9998

AlCr1:1	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	8.11012	0.1042	0.16089	0.0037	1.17726	0.02272	0.9993
283 K	8.34598	0.06836	0.13805	0.00149	1.09116	0.01047	0.9988
293 K	8.17381	0.0886	0.11272	0.00157	1.13705	0.01374	0.9991
303 K	8.73075	0.1291	0.11211	0.00157	0.9551	0.01078	0.9996

AlCr2:3	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	7.10414	0.07749	0.19859	0.00386	1.14051	0.01872	0.9995
283 K	7.45902	0.08426	0.15352	0.00258	1.11888	0.01597	0.9995
293 K	7.78591	0.07813	0.13902	0.00179	1.07432	0.01179	0.9997
303 K	7.58233	0.08552	0.30903	0.00563	0.91385	0.01333	0.9998

A2.3 N₂

NOTT-300(Cr)	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	6.66067	0.19237	0.0677	0.0021	1.02788	0.00463	0.9974
283 K	6.94209	0.15268	0.0575	0.00213	0.97511	0.00219	0.9982
293 K	6.7686	0.2084	0.03969	0.00111	0.98465	0.00235	0.9989
303 K	6.38429	0.10592	0.04222	0.00104	1.00526	0.00337	0.9983

AlCr2:1	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	7.57605	0.25716	0.06165	0.00273	0.99018	0.01736	0.9978
283 K	7.07017	0.39287	0.05656	0.01639	0.92755	0.08294	0.9982
293 K	6.89731	0.28409	0.04791	0.00927	0.94304	0.02712	0.9986
303 K	7.01389	0.23492	0.04644	0.01612	0.69032	0.03849	0.9989

AlCr1:1	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	2.10808	0.37127	0.58895	0.16063	0.82592	0.0461	0.9958
283 K	1.68858	0.40445	0.49484	0.07315	0.9139	0.05825	0.9964
293 K	2.84352	1.32066	0.17143	0.09257	0.84874	0.03921	0.9981
303 K	0.80279	0.15592	1.10224	0.42491	1.00238	0.09873	0.9976

A2.4 CO

NOTT-300(Cr)	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	8.63154	0.13673	0.08226	0.00143	0.97888	0.00271	0.9999
283 K	7.85809	0.81201	0.08368	0.02386	1.02194	0.01311	0.9999
293 K	6.75778	0.14098	0.05813	0.00112	0.99208	0.00233	0.9999
303 K	4.32843	0.72511	0.09259	0.00638	0.96871	0.00334	0.9994

AlCr2:1	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	8.21578	0.29483	0.08888	0.00189	0.97044	0.00392	0.9995
283 K	8.85139	0.38294	0.06859	0.00839	0.95415	0.00933	0.9991
293 K	8.73006	0.24748	0.05756	0.00234	0.89855	0.00638	0.9989
303 K	7.85368	0.19483	0.0406	0.01022	0.92925	0.00517	0.9992

A2.5 O₂

AlCr2:1	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	7.96102	0.83283	0.05688	0.00775	1.00897	0.00829	0.9991
283 K	7.52824	0.73528	0.05053	0.00186	0.94286	0.00735	0.9987
293 K	6.96413	0.63872	0.04678	0.00202	0.91726	0.00766	0.9992
303 K	6.27368	0.70372	0.04325	0.00875	0.96503	0.00699	0.9989

A2.6 C₂H₂

NOTT-300(Cr)	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	7.48253	0.03203	37.31174	2.90493	1.46162	0.02932	0.9995
283 K	7.46894	0.04138	19.10463	1.25401	1.47369	0.02777	0.9996
293 K	7.53466	0.05859	9.22245	0.52045	1.44827	0.02573	0.9997
303 K	7.86215	0.05644	0.1217	8.5237 E ⁻⁴	1.06816	0.00812	0.9999

AlCr2:1	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	7.74723	0.03905	29.56213	2.16274	1.4458	0.02614	0.9994
283 K	7.8426	0.05167	14.03219	0.84782	1.41415	0.02358	0.9995
293 K	8.05945	0.09408	6.33525	0.40432	1.34651	0.02595	0.9994
303 K	8.84415	0.22614	2.57375	0.20376	1.23061	0.02934	0.9993

AlCr1:1	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	7.11488	0.02893	15.65302	0.65535	1.35308	0.01621	0.9998
283 K	7.1887	0.03617	12.75087	0.5686	1.45615	0.01904	0.9998
293 K	7.34162	0.06363	7.25714	0.38314	1.42607	0.0236	0.9997
303 K	7.53281	0.09793	3.72668	0.19077	1.35459	0.0223	0.9997

AlCr2:3	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	6.2287	0.04037	13.2469	0.79025	1.24815	0.02167	0.9996
283 K	6.4934	0.04153	10.1600	0.49711	1.33346	0.01965	0.9997
293 K	6.7498	0.06983	6.68134	0.39802	1.39727	0.02618	0.9996
303 K	7.222	0.10405	3.50477	0.19117	1.29042	0.02256	0.9997

A2.7 C₂H₄

NOTT-300(Cr)	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	6.97839	0.03705	9.30707	0.36615	1.28037	0.01607	0.9998
283 K	6.85065	0.038	5.27408	0.14698	1.24769	0.01153	0.9999
293 K	6.84499	0.05077	3.01874	0.078	1.20584	0.01021	0.9999
303 K	6.90029	0.07726	1.79969	0.05152	1.15776	0.01008	0.9999

AlCr2:1	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	7.11029	0.0337	4.96236	0.11419	1.13554	0.00877	0.9999
283 K	7.11116	0.03971	3.42081	0.07249	1.09194	0.00774	0.9999
293 K	5.34113	0.05287	3.13926	0.1107	0.95907	0.0108	0.9998
303 K	6.84057	0.05294	1.5142	0.02733	1.04514	0.00557	0.9999

AlCr1:1	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	6.37872	0.02284	6.26233	0.12301	1.34457	0.00824	0.9999
283 K	6.72809	0.07892	2.72637	0.10333	1.24057	0.01472	0.9998
293 K	6.64088	0.13404	1.94319	0.10382	1.23469	0.01974	0.9997
303 K	6.72905	0.1905	1.27962	0.07689	1.17089	0.01904	0.9997

AlCr2:3	q_{sat}	Standard error	b	Standard error	v	Standard error	Adj. R^2
273 K	5.36582	0.03119	5.54251	0.16523	1.19655	0.01139	0.9999
283 K	5.66515	0.02036	3.34943	0.04441	1.18386	0.00503	0.9999
293 K	5.87423	0.06588	2.27874	0.07438	1.19145	0.01204	0.9999
303 K	5.94531	0.14256	1.5173	0.08428	1.23176	0.01951	0.9998

A2.8 C₂H₆

NOTT-300(Cr)	q _{sat}	Standard error	b	Standard error	v	Standard error	Adj. R ²
273 K	6.03411	0.06827	6.10892	0.39045	0.95239	0.02046	0.9995
283 K	6.85065	0.038	5.27408	0.14698	1.24769	0.01153	0.9999
293 K	6.97504	0.04603	2.2254	0.0426	1.0652	0.00652	0.9999
303 K	5.45454	0.04664	2.6819	0.07468	1.02416	0.0094	0.9999

AlCr2:1	q _{sat}	Standard error	b	Standard error	v	Standard error	Adj. R ²
273 K	5.87008	0.08065	4.62708	0.29292	0.89172	0.0181	0.9995
283 K	5.57361	0.07074	3.9684	0.209	0.93344	0.01577	0.9996
293 K	5.34113	0.05287	3.13926	0.1107	0.95907	0.0108	0.9998
303 K	5.08221	0.04323	2.55395	0.06801	0.97592	0.00817	0.9999

AlCr1:1	q _{sat}	Standard error	b	Standard error	v	Standard error	Adj. R ²
273 K	6.07672	0.21456	1.06056	0.07313	0.84382	0.01522	0.9997
283 K	6.13259	0.15256	1.08914	0.0535	0.92252	0.0119	0.9998
293 K	5.68186	0.07257	1.36702	0.03848	1.01154	0.00801	0.9998
303 K	4.90128	0.04203	1.7058	0.03611	1.21236	0.00756	0.9999

AlCr2:3	q _{sat}	Standard error	b	Standard error	v	Standard error	Adj. R ²
273 K	4.38181	0.15723	1.66015	0.14578	0.82642	0.02142	0.9995
283 K	4.71484	0.0678	1.69686	0.06039	0.86946	0.00917	0.9999
293 K	5.18767	0.02394	3.1089	0.05059	1.12418	0.00585	0.9999
303 K	4.83821	0.01723	1.94526	0.01845	1.0205	0.00294	0.9999

Appendix 3 – Van't Hoff Linear Fittings

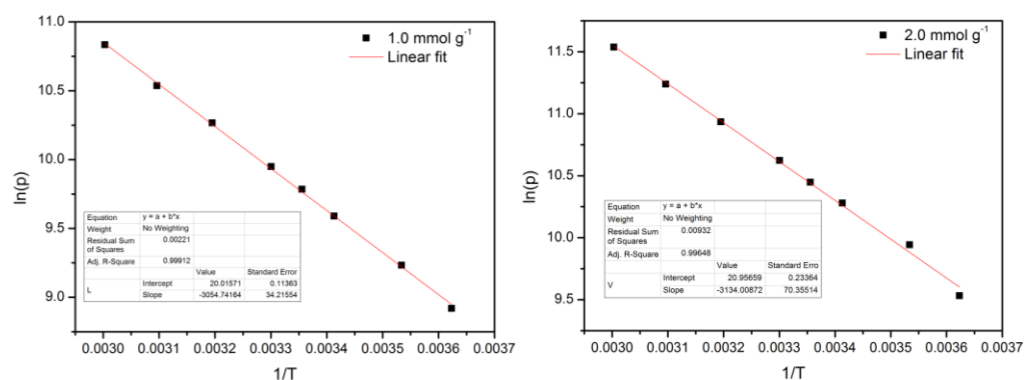
The heats of adsorption and entropies for the gas sorption experiments carried out were calculated using the van't Hoff isochore. The isotherms recorded at 273 – 303 K (or higher, if the data is available) were fitted to the van't Hoff equation.

$$\ln(p) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

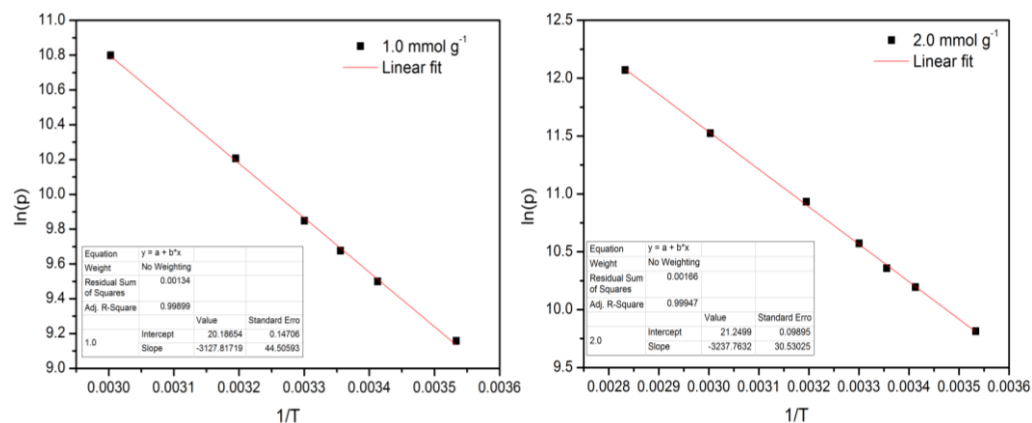
A plot of $\ln(p)$ vs. $1/T$ allows the enthalpy and entropy to be determined, examples of linear fitting plots at 1.0 and 2.0 mmol g⁻¹ are shown below.

CO₂

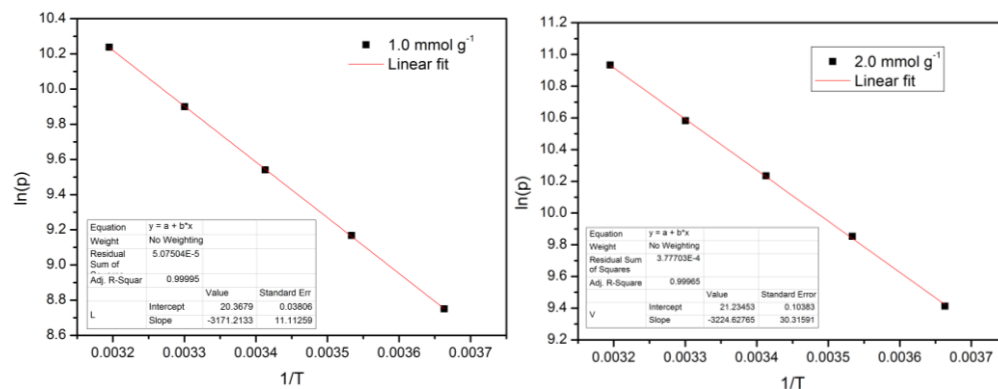
NOTT-300(Cr) –



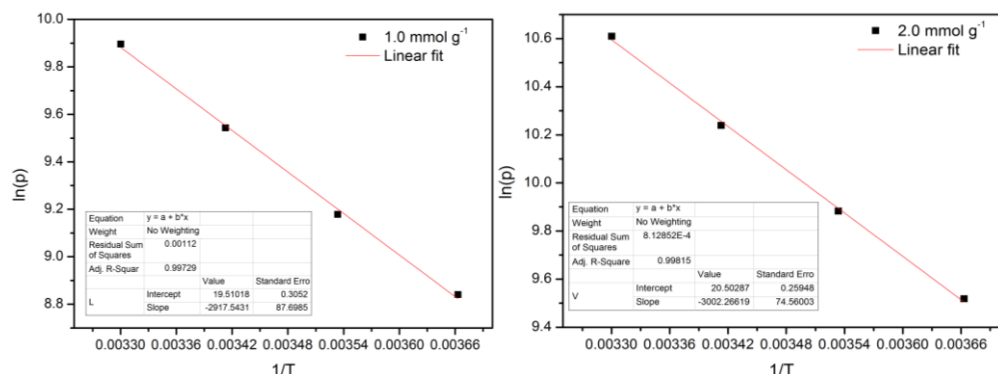
AlCr2:1 –



AlCr1:1

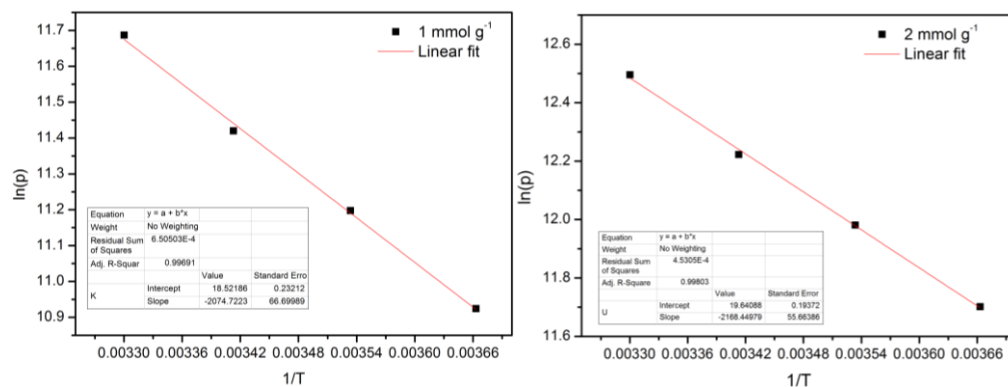


AlCr2:3

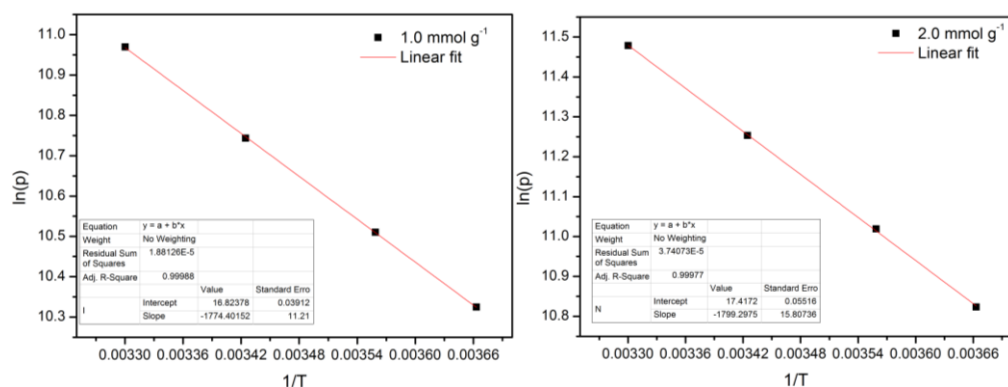


CH₄

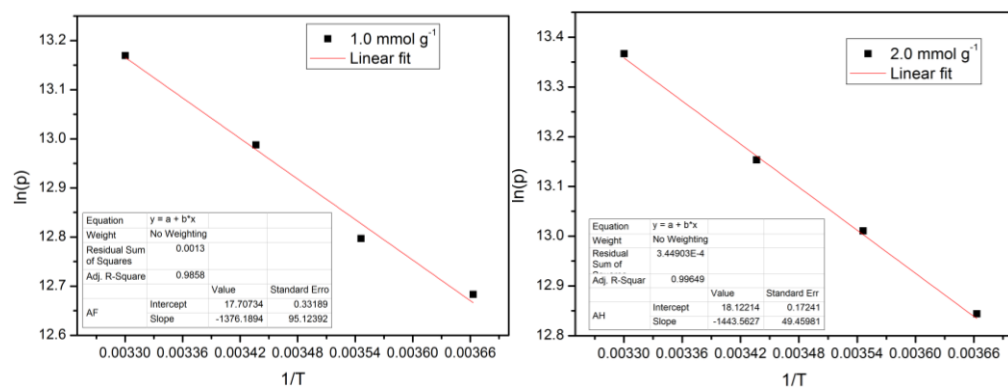
NOTT-300(Cr)



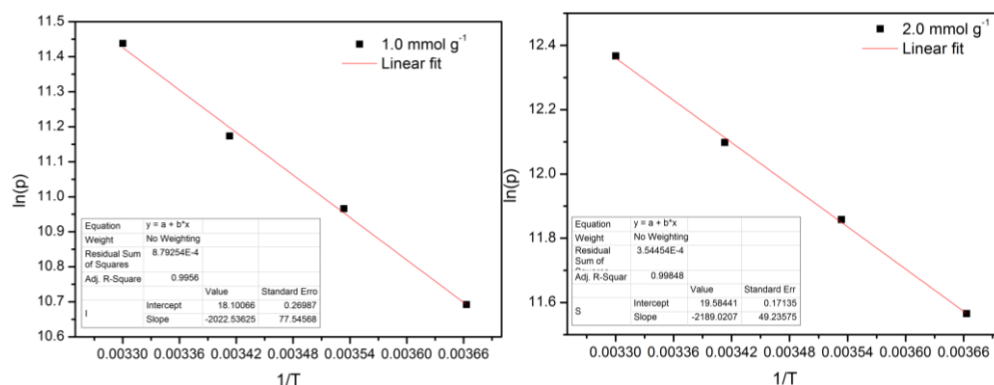
AlCr₂:1



AlCr₁:1

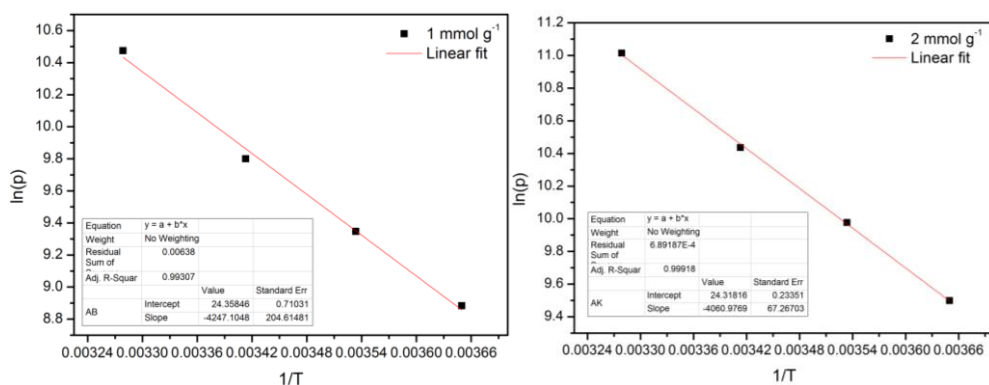


AlCr₂:3

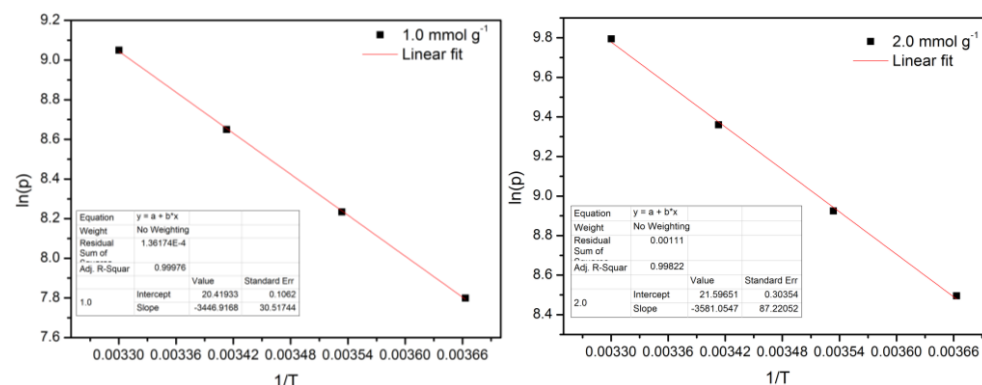


C₂H₂

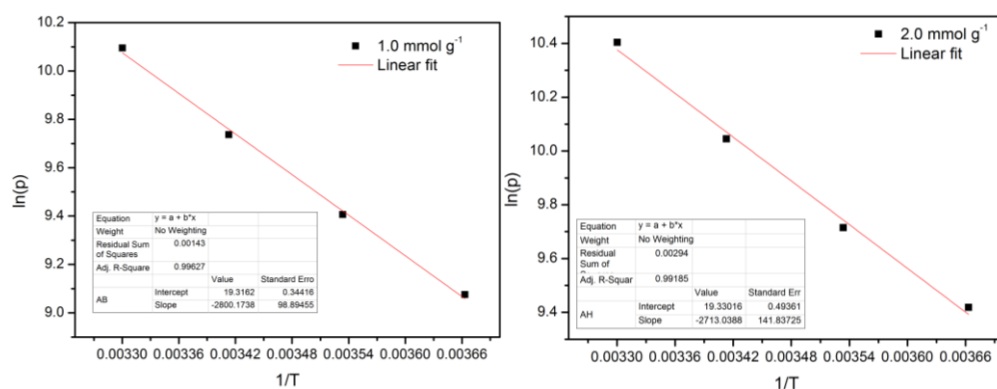
NOTT-300(Cr)



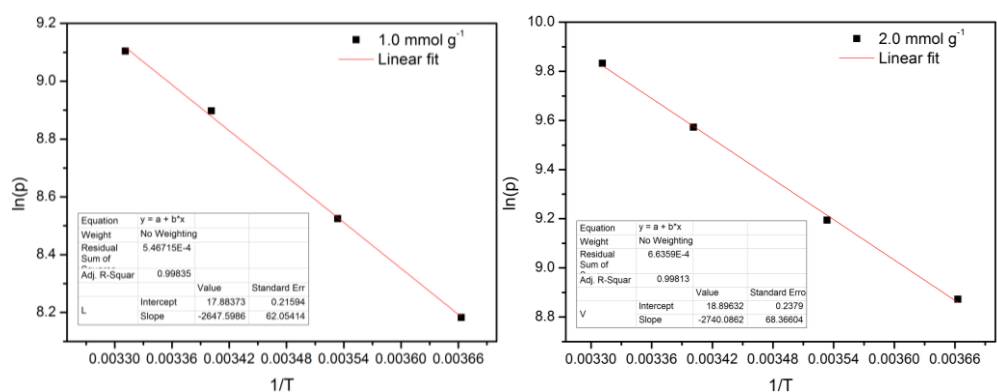
AlCr₂:1



AlCr1:1

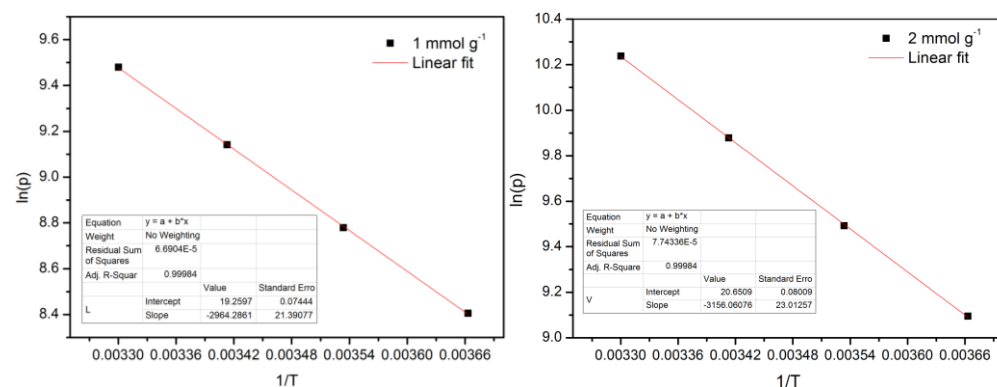


AlCr2:3

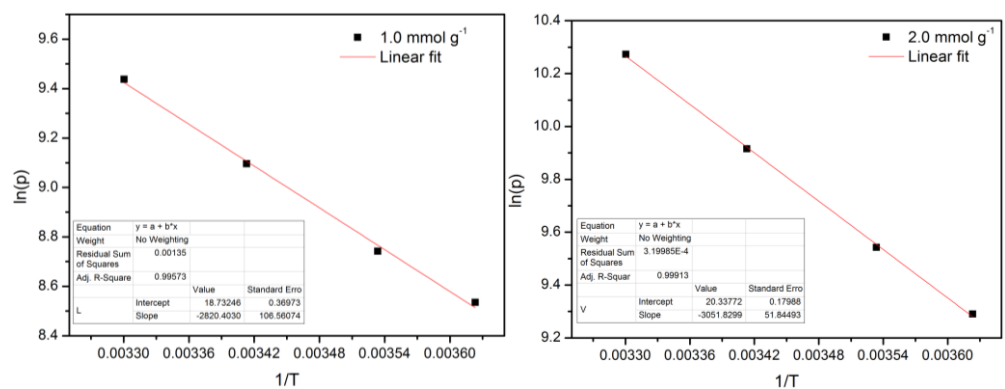


C₂H₄

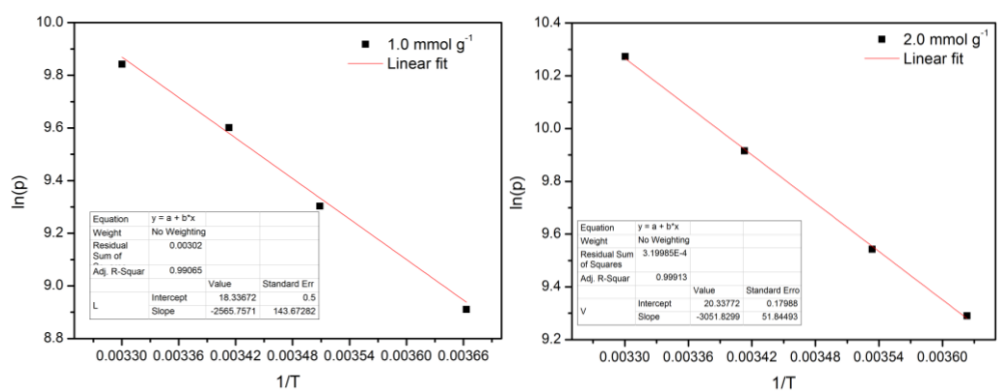
NOTT-300(Cr)



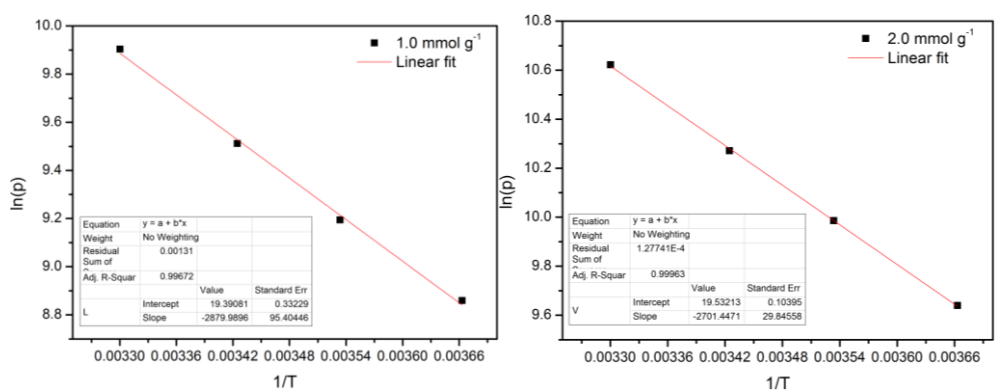
AlCr2:1



AlCr1:1

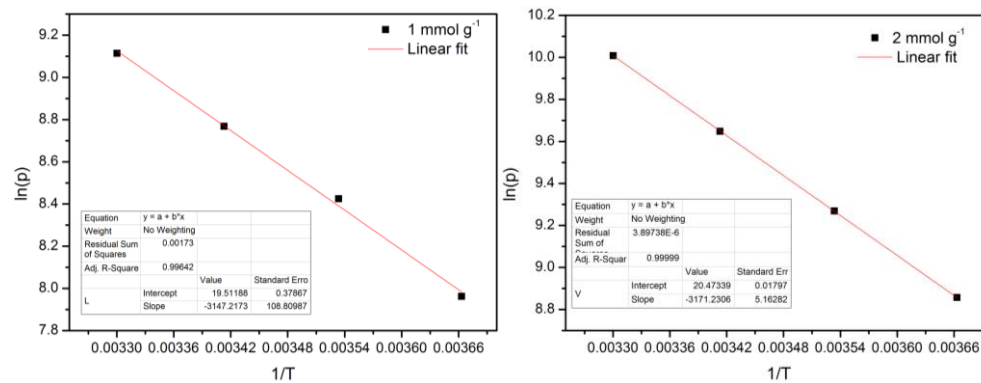


AlCr2:3



C₂H₆

NOTT-300(Cr)



AlCr₂:1

