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# Abstract

Abstract is here.

# Acknowledgements

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# 1 Exploring the impact of material form on adsorption measurements

## 1.1 Introduction

An adsorbent cannot be used in an industrial process in its raw powder form. The small crystals which are normally the synthesis product of such a material would not be suited for direct use and need to be transformed into hierarchically porous structures.

Therefore, adsorbents are usually shaped into pellets, a process which introduces a range of benefits, such as improved flow regimes, better thermal management and material containment. The shaping process is needed not just for stabilising the small particles, but also to impart the resulting pellet with a high enough mechanical resistance to withstand the stresses imposed by the high flow encountered in an industrial bed.

The shaping process is therefore a crucial step towards the large-scale use of an adsorbent material. Even for commonplace adsorbents such as carbons and zeolites, the optimum binding compound and the shaping process itself are the subject of extensive research. Often, the procedure is tailored for individual material and application.

In an ideal setting, the process has limited effects on the properties of the material. However, this is often not the case, as shaping can degrade or improve adsorption performance. After a short introduction to shaping, this chapter explores the variability introduced by the binder in three topical MOFs: UiO-66(Zr), MIL-100(Fe) and MIL-127(Fe), which have been selected for their good stability and well-studied adsorption behaviour. The alumina shaped variant of these MOFs is compared to the original powder material, with regard to the adsorption of a series of common gasses and vapours. Microcalorimetry in conjunction with 8 gas probes has been used to get an in-depth picture of the change in surface energetics, with a separate study of adsorption of water and methanol vapour to examine changes in hydrophobicity. Particular behaviours are then highlighted and discussed.

Finally, a previous study on the same materials shaped with a poly-vinyl alcohol (PVA) binder is extended to vapour adsorption and the entire dataset is processed to obtain an overview of the impact of a hydrophobic and a hydrophilic binder on adsorption performance.

## 1.2 Shaping in context

In order to use an adsorbent in an industrial setting such as the beds and columns common in PSA (pressure swing adsorption) and TSA (temperature swing adsorption) processes, a pelletized form of the material is required.<sup>(1)</sup>

The kinetics of the adsorption process are generally improved by the multi-scale pore size distribution afforded through shaping. Capacity per mass of pellet is expected to

decrease due to the addition of a non-porous component, but the difference should be small and should not arise due to effects such as pore blocking or pore filling with the binder material. Furthermore, the densification effect is expected to lead to better performance on a volume basis. Finally, binder addition should not influence the chemical properties of the adsorbent, and preserve the original interactions with the adsorbate. With a judicious choice of binding material, the resulting pellet should outperform the powder.

For carbons, binders such as pitch, polymers (CMC, PVA) or even non-porous carbon black are commonly used.<sup>(2)</sup> Often, a combination of binders is used, each with a different task during the pelletization process.<sup>(3)</sup> The process itself consists of extrusion of the particle-binder slurry and then hardening either through temperature, cross-linking or chemical treatment. Other methods, such as spray-drying or granulation can similarly be used.<sup>(4)</sup>

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For zeolites, inorganic binders are more prevalent, with silica, alumina and clay binders commonly used in industry. It has been shown<sup>(5,6)</sup> that the choice of binder can introduce large property variations, ranging from loss of porosity and structure to the enhancement of the desired reactivity and selectivity through changes in the acid site density or ion migration.

The shaping of MOFs has been attempted with a wide range of binders and methods. Methods such as granulation, spray-drying or extrusion have all been successfully employed to create MOF pellets.<sup>(7)</sup> Monoliths have also been shown to be an effective way for shaping purposes, either through impregnation<sup>(8)</sup> or through support on alumina.<sup>(9)</sup> Surprisingly, compression<sup>(10)</sup> or even simple air drying of MOF slurries<sup>(11)</sup> have also shown good results. Note that the ZIF-8 monolith prepared through the latter method had a three times larger volumetric specific surface area than the conventional powder.

The connection between MOF and binder is also of crucial importance for membranes. The MOF-polymer interface has been shown<sup>(12)</sup> to be subject to a complex interplay of interactions between the organic chains and the crystal surfaces. These effects can be striking enough to warrant further research into MOF-polymer hybrids,<sup>(13)</sup> with the aim of combining the unique attributes of both materials.

Previous work from this group<sup>(14)</sup> has analysed the impact of PVA shaping on a series of MOFs. It was shown that the binder did introduce some specific effects, such as a protection effect on the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  in MIL-127(Fe), as well as a curious gating effect seen on butane adsorption on MIL-100(Fe), likely due to polymer chains covering pore entrances. Otherwise, the shaping imparted good performance to the shaped samples, with almost no capacity loss on a mass basis. Unfortunately, the use of a polymer limited the activation temperature of the samples to a maximum of 150 °C.

In this work we have selected the same series of “topical” MOFs and have investigated the influence of a different shaping method, namely the use of alumina binder, on their adsorption properties.

The UiO-66(Zr) MOF and its derivatives are well known due to their stability, both in regards to temperature and chemical compounds.<sup>(15)</sup> It is composed of Zr6-oxo clusters which are connected with benzene dicarboxilate (BDC) linkers to form a face-centered

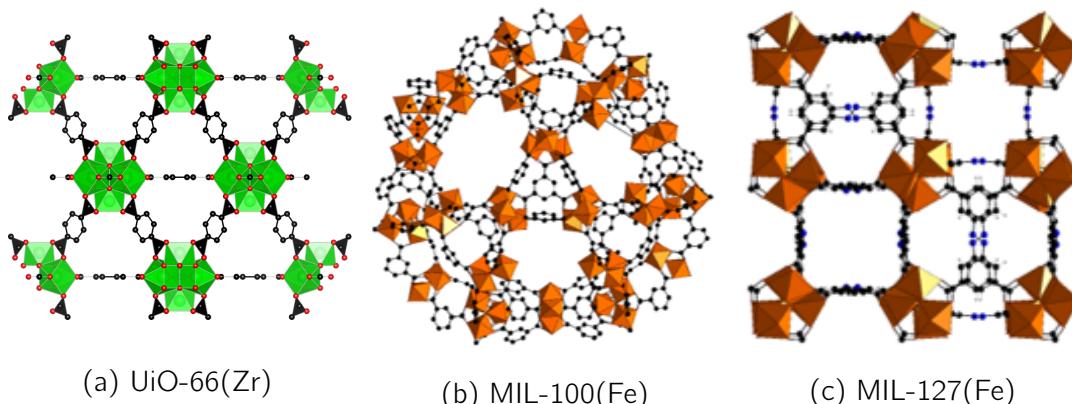


Figure 1.1: The unit structures of the investigated MOFs. The colour coding is as follows: Zr polyhedra in green, Fe octahedra in brown, C in black, O in red, N in blue. Hydrogen atoms are omitted for clarity.

cubic framework. It has shown promise<sup>(16)</sup> in use for gas adsorption applications.

MIL-100(Fe) is a MOF which uses the benzene tricarboxilate (BTC) linker in conjunction with trimeric iron (III) octahedral clusters.<sup>(17)</sup> The framework assembles in hybrid supertetrahedra which leads to very large pore sizes. The iron trimers are coordinated with anions and have shown a propensity to partially reduce to a divalent  $\text{Fe}^{2+}$  state, exposing a naked metal site in the process.<sup>(18)</sup>

The last material, MIL-127(Fe), originally reported by Liu et al. is a MOF built from the same metal (III) octahedra trimers as MIL-100(Fe), but using the 3,3',5,5'-azobzenetetracarboxylate (TazBz) linker, to produce a framework with the (soc) topology. This material has shown promise<sup>(20)</sup> for large scale synthesis. Furthermore, due to its alternating hydrophobic/hydrophilic microporous systems, it has been shown to be of interest for multiple applications such as catalysis or  $\text{CO}_2$  capture.<sup>(21)</sup>

The structures of the three materials can be seen in Figure 1.1.

## 1.3 Synthesis, shaping and characterisation

### 1.3.1 Material Synthesis

The synthesis of these MOFs is well described in literature, as it has been previously reported for UiO-66(Zr)<sup>(15)</sup> and MIL-100(Fe).<sup>(22)</sup>

The UiO-66(Zr) and MIL-100(Fe) powders have been synthesised at the Korea Research Institute of Chemical Technology (KRICT) according to the methods previously referenced. Complete details of the synthesis method can be found in the related publication<sup>(23)</sup> and in Appendix

Appendix

### 1.3.2 Shaping Procedure

The shaping of the samples also took place at KRICT and was done using a wet granulation method. In the case of the alumina binder, the MOF powder was mixed with the previously prepared mesoporous  $\rho$ -alumina with water added as the dispersing medium. For the PVA binder, the MOF powder was instead added to a solution of ethanol solution containing a polymer mixture of polyvinyl groups such as polyvinyl alcohol and polyvinyl butyral. The resulting mixture was shaped into beads using a hand-made pan granulator. During the process, the spheres were sprayed with the respective solvent in order to achieve desired size. The beads were then sieved and rolled using a roller machine to enhance their spherical shape. Finally, the prepared samples were dried at 303 K for 12 h to remove all residual solvent. The resulting beads were near spherical in shape, with a diameter between 2 mm to 2.5 mm.

### 1.3.3 Characterisation of powders and pellets

The primary interest of the study was observing differences in adsorption properties between the powder and the shaped materials.

Thermogravimetric analysis was used to verify that the binder did not change the thermal stability of the materials and, in the case of the PVA variant, to ensure that the activation temperature chosen did not induce polymer decomposition. The TGA method is described in detail in Appendix 1.

### 1.3.4 Sample activation for adsorption

The materials were pre-treated before all adsorption experiments by activation at high temperature under secondary vacuum for 16 hours. The activation temperature was specific to each solid: 200 °C for UiO-66(Zr), 150 °C for MIL-100(Fe) and 150 °C for MIL-127(Fe).

## 1.4 Results and discussion

### 1.4.1 Thermal stability

In order to check if the shaped samples have not undergone bulk structural changes

The process of shaping did not have any impact on the thermal stability of the investigated MOFs, as evidenced by the TGA curves (Figure 1.2). The primary mass loss occurs in a 10 °C range for all powder-pellet pairs. Shaped samples are expected to have a smaller percentage mass loss overall due to the addition of the temperature inert alumina.

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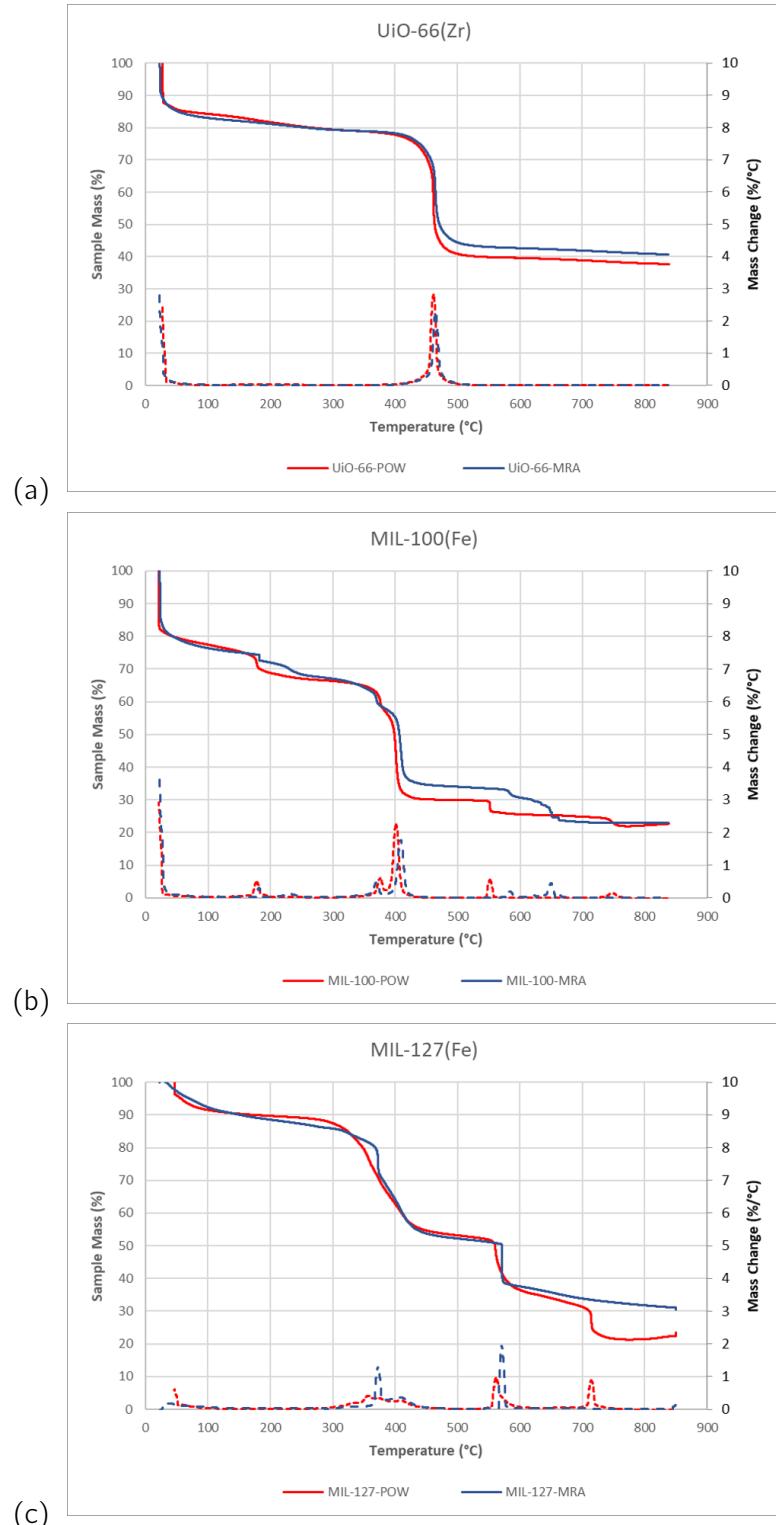


Figure 1.2: High resolution TGA curves recorded under argon on (a) UiO-66(Zr), (b) MIL-100(Fe) and (c) MIL-127(Fe). The original powders are depicted in red and the shaped material in blue.

### 1.4.2 Adsorption isotherms at 77K and room temperature

Nitrogen sorption isotherms measured at 77 K have been measured on both powder and  $\rho$ -alumina pellets, with the dataset presented in Figure 1.3.

The isotherms can be processed to yield properties such as specific surface area and pore volume for the powders and the pellets.

Table 1.1: Properties of the studied powders and pellets

MOF	form	BET surface area	Pore volume	Bulk density
UiO-66(Zr)	powder	903	0.38	0.3192
	$\rho$ -alumina	619	0.24	0.4724
MIL-100(Fe)	powder	1928	0.78	0.2165
	$\rho$ -alumina	1451	0.6	0.3512
MIL-127(Fe)	powder	1400	x	0.412
	$\rho$ -alumina	1266	0.49	0.526

As expected, the specific surface area of the shaped samples is decreased compared to the corresponding powder. While in the case of MIL-127(Fe) the BET area is only 10% lower, for the MIL-100(Fe) and UiO-66(Zr) materials a larger drop is seen, of 25% and 31%, respectively. Another property which can be used to corroborate the effects of shaping is micropore volume, calculated as the volume of nitrogen adsorbed at a  $p/p^0$  of 0.2. A similar capacity decrease can be seen here with a 36%, 23% and x% seen in UiO-66(Zr), MIL-100(Fe) and MIL-127(Fe) respectively.

The decrease in both surface area and micropore volume is too large for it to be a consequence of the presence of non-porous binder. It is therefore theorised that some structure degradation must have occurred in the pelletisation process.

Observation of the physisorption curves sheds light on the further impact of the alumina binder on the materials chosen. The shapes of all isotherms are visually similar, with the pellet ones shifted downwards due to the aforementioned structure degradation. In both powders and pellets, the increased uptake after 0.9  $p/p^0$  is a sign of condensation in very large pores or voids, which can be attributed to intra-pellet spaces and crystal agglomeration. In the MIL-127(Fe) pellets, a narrow hysteresis curve is seen, which closes at a  $p/p^0$  of 0.5. This curve corresponds to capillary condensation in a pore size of around 4 nm. This pore width is too small to be a sign of inter-pellet voids and therefore must be a consequence of the shaping process.

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### 1.4.3 Water adsorption

The shape of the water vapour isotherm will be an indication of the hydrophilicity of the material. By itself, alumina is a hydrophilic substance, with a contact angle of 10°. It is expected that the addition of the binder will therefore increase the affinity of the resulting pellet towards water.

# 1 Exploring the impact of material form on adsorption measurements

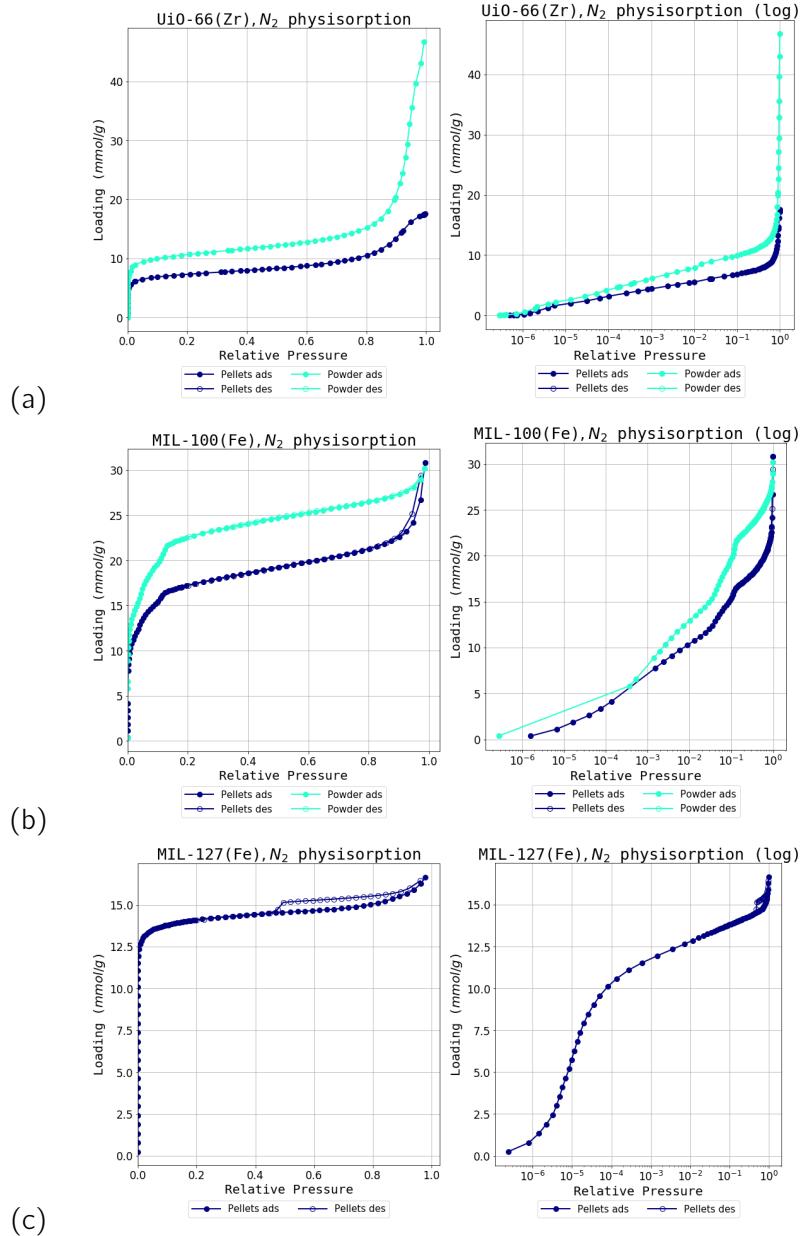


Figure 1.3: Nitrogen isotherms at 77K for (a) *UiO-66(Zr)*, (b) *MIL-100(Fe)* and (c) *MIL-127(Fe)*. The powder sample is in light blue while the  $\rho$ -alumina sample in dark blue. Logarithmic graphs of the isotherms are on the right for clarity of the low pressure region.

Looking at the resulting adsorption measurements one can see the typical downwards shift of the pellet isotherms resulting from structure degradation. However, changes in the interaction of the MOF with water do not seem to be highlighted. The low relative pressure region ( $p/p^0 < 0.3$ ) should be particularly indicative of any such changes, but an almost complete overlap can be seen in this region. In particular, the UiO-66(Zr) isotherms have a surprising amount of similarity, considering the loss of capacity seen in N<sub>2</sub> physisorption and room temperature adsorption experiments.

It can be therefore concluded that overall, the addition of alumina has not influenced the behaviour towards water for the materials studied. The full water adsorption isotherms can be found in Figure 1.4.

#### 1.4.4 Room temperature gas adsorption and microcalorimetry

Combining microcalorimetry with adsorption manometry is a powerful technique which can give an insight into the strength of the interactions during the adsorption process, by directly measuring the differential heat. Even though the different contributions to the overall enthalpy curve cannot be decoupled from the individual sources, such as gas-adsorbent interactions, gas-gas interactions or confinement effects, it is well suited for observing the effect of a process or treatment such as shaping on the properties of a MOF.

A wide variety of probe gasses has been chosen for adsorption at 303 K: N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub>. The range of adsorbates chosen allows different effects to be investigated. The adsorption of saturated hydrocarbons with an increasing carbon number (C1-C4) can be assumed to be driven strictly by Van-der-Waals forces, due to the shielding effects of the hydrogen atoms. Differences in the uptakes of these gasses will point to loss of porosity or crystallinity. An assymetric capacity loss with the larger molecules will point to size exclusion effects induced by the binder, such as particle coating, pore filling or pore obstruction. The other probes have been chosen for their individual properties which can shine light on other specific interaction types present during the adsorption. Carbon monoxide is a slightly dipolar molecule which has the ability to interact with other charges in the pores. It also can highlight CUS (coordinatively unsaturated sites) generated through defects, reduction or open metal sites due to its propensity for  $\pi$  backbonding coordination. This electron transfer process also can result in complexation with molecular orbitals in systems with  $\pi$  bonds such as alkenes and alkynes. Propylene is used as a probe gas for this purpose. Carbon dioxide is a highly quadrupolar molecule which will be strongly adsorbed in polar pore environments. Changes in the adsorption behaviour of CO<sub>2</sub> will shed light on such surface changes and can even be used as a predictor of hydrophobicity.<sup>(21)</sup> Finally, N<sub>2</sub> is a staple adsorbent for material characterisation when used at 77K. The molecule is a slight quadrupole and has also been shown to chelate to some transitional metals in an analogue fashion to CO.

To eliminate the influence of kinetic and diffusion effects on the experiments, care has been taken to allow time for complete equilibration of both pressure and calorimeter signal.

# 1 Exploring the impact of material form on adsorption measurements

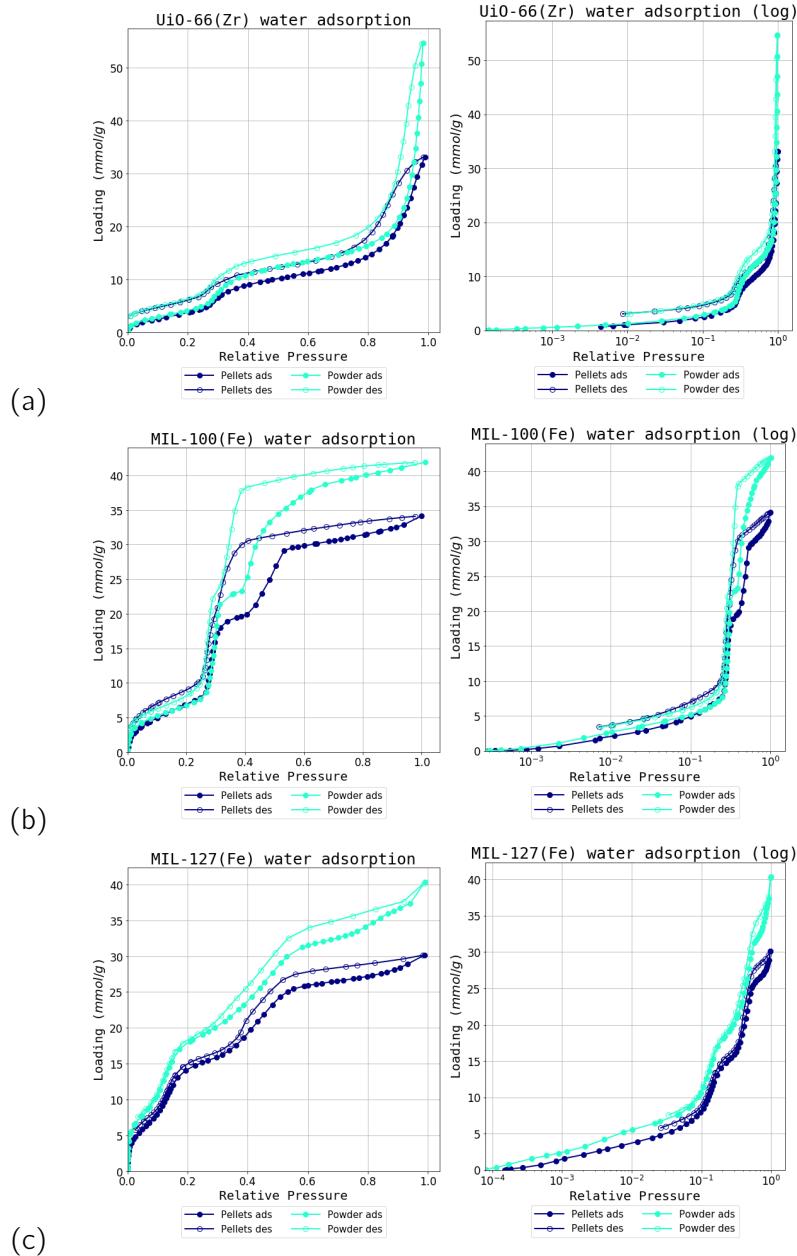


Figure 1.4: Water adsorption isotherms (a)  $\text{UiO-66}(\text{Zr})$ , (b)  $\text{MIL-100}(\text{Fe})$  and (c)  $\text{MIL-127}(\text{Fe})$ .

The powder sample is in light blue while the  $\rho$ -alumina sample in dark blue. Logarithmic graphs of the isotherms are on the right for clarity of the low pressure region.

After collecting the combined isotherm enthalpy data, three indicators have been chosen to best represent the effects of shaping: initial enthalpy of adsorption, initial Henry constant and maximum capacity. These numeric performance indicators have been calculated programmatically in Python using a specially developed high throughput package. The initial enthalpy of adsorption extrapolated at zero coverage is a measure of the interaction with highest energetic sites on the MOF surface. Conversely, the  $K_H$  obtained by applying the linear Henry model at the lowest loading points is also an indication of adsorption in the pores before any layering or adsorbate-adsorbate interaction comes into effect. The  $K_H$  was calculated by fitting the virial adsorption model (Equation 1.1) to the isotherm. The last indicator, maximum capacity, was taken as the loading attained when the isotherm reached a plateau. In the case of probes where the plateau was outside the range of pressure of the instrumentation ( $>50$  bar), the loading at the highest available pressure was considered as a suitable approximation. The three KPIs (key performance indicators) have then been compared side by side on both the powder and shaped samples.

$$\ln \frac{n}{P} = \ln K_H + An + Bn^2 \dots \quad (1.1)$$

The complete dataset of adsorption isotherms, in the basis of both mass and volume can be found in the Supplementary Information (Figures 1 , 2 and 3 ).

### **UiO-66(Zr)**

A visual inspection of the enthalpy curves on UiO-66(Zr) show it to have a relatively homogenous surface, with flat profiles being common.

The KPI graphs show very similar values for both Henry's constant and initial enthalpy of adsorption. It is therefore apparent that the shaping process did not change the interaction of the adsorbate with the MOF surface.

The maximum capacity graphs show a more interesting trend. When using small adsorbates such as N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>, the shaped samples have a similar performance on a mass basis and, due to the densification process, better capacities on a volume basis. Starting with ethane, the maximum capacity starts to decrease, with the performance worsening with increasing molecule size. On hydrocarbons with a carbon number of 3 and 4, both mass basis and volume basis capacity is decreased compared to the original powder. Carbon monoxide is an apparent outlier to this trend, with a decreased maximum capacity and a small molecular size. This size exclusion effect could be explained by the coating of crystal surfaces with the alumina binder. It could be argued that instead of size exclusion, the decrease is due to a decrease in pore volume, and that the isotherms of the low molecular weight gasses will diverge at higher pressures as the pores are filled. A counterargument for this hypothesis is that on CO a divergence is observed while the isotherm is still in the Henry's region and in the case of CO<sub>2</sub>, the plateau is reached with no differences between the powder and the pellet.

Overall, the shaping performance of UiO-66(Zr) is reasonable, as long as only small adsorbates are used.

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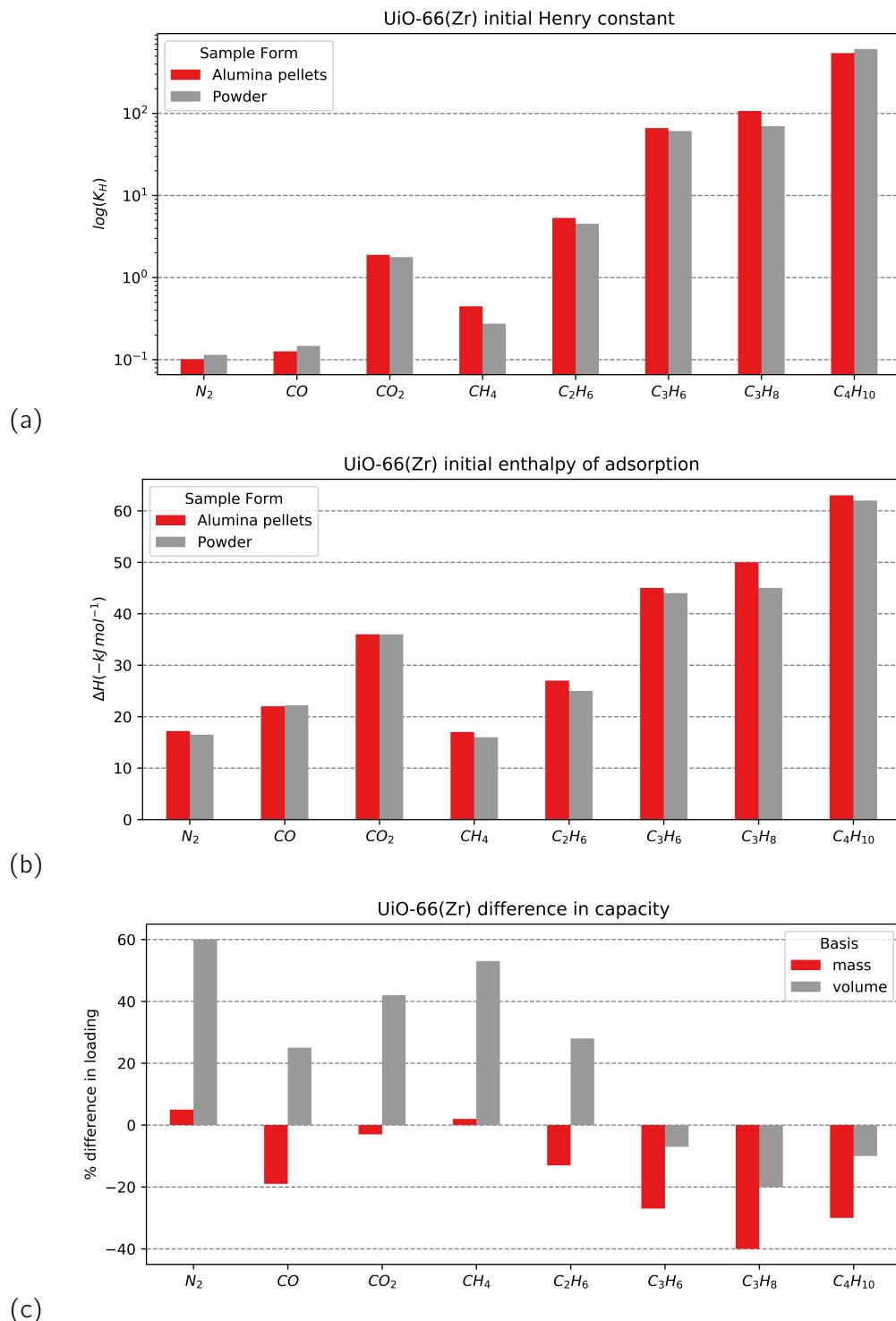


Figure 1.5: UiO-66(Zr) analysis

### MIL-100(Fe)

The enthalpy profiles on MIL-100(Fe) are less homogenous than the ones on UiO-66(Zr). Some effects can be seen with probes which can interact with the partially reduced Fe(II) atom, such as carbon monoxide and propylene. Indeed, when comparing both the initial Henry constants and enthalpy of adsorption, for CO and C<sub>3</sub>H<sub>6</sub>, these are higher than the values obtained on UiO-66(Zr). With initial enthalpy of adsorption for CO of around 45 kJ mol<sup>-1</sup>, the value falls into the range of previous<sup>(18)</sup> results for interactions with such Fe(II) CUS.

Comparing the powder and shaped variants, there are no apparent differences between the two. The only discrepancy, which can be seen on the nitrogen  $K_{H,init}$  follows as a result of an ill-fitting virial parameter, and can be assumed an error after observing the isotherm overlap directly. It could be theorised that by activation at a higher temperature (250 °C), the percentage of iron trimers which would undergo reduction will increase and a larger adsorption enthalpy could be observed. However, the activation temperature was chosen to maintain comparability with a previous study.<sup>(14)</sup>

The maximum loading differences of the MIL-100(Fe) show a very homogenous distribution. On all probes tested, a fixed capacity loss of between 10-20% can be seen on a mass basis. However, the increase in density afforded by the compression during pelletisation leads to a compensation in performance as can be seen in Figure 1.6c.

We can conclude that MIL-100(Fe) is almost unaffected by alumina shaping. A slight loss in maximum capacity on a mass basis is compensated by a pronounced densification, which is desirable in an industrial setting.

### MIL-127(Fe)

The isotherms on MIL-127(Fe) show similar behaviour as the MIL-100(Fe) material, although with a sharper uptake as a result of the smaller pores. Enthalpy profiles are also influenced by the similar interactions with the iron trimers leading to higher initial heats of adsorption on CO and C<sub>3</sub>H<sub>6</sub>. An unexpected increase in the heat of adsorption is seen with butane adsorption (Figure 1.7a). Due to the dual pore type in the MIL-127(Fe) structure, it is likely that adsorption first commences in the small (~6 Å) channels and then, at higher pressures, intrusion into the larger cage-type pores is possible through the narrow apertures of ~3 Å. The confined cages have an increased interaction with the molecule which leads to the higher enthalpy values.

When observing the comparison between the powder and the pellet variant, a large difference in the initial  $K_H$  on CO stands out as the only major change. The value of the initial enthalpy of adsorption does not follow the same pattern. However, visual inspection of the isotherm (Figure 1.7b) and the enthalpy curve shows that the energy of adsorption corresponding to interactions with the more active sites is maintained for a larger pressure range. This points to the higher preponderence of such sites in the powder variant. A similar offset can be seen in the propylene enthalpy at very low pressures, but this is not reflected in the shape of the isotherm. The weaker complexation strength and the larger size of the molecule likely limits the effect seen in the carbon monoxide

1 Exploring the impact of material form on adsorption measurements

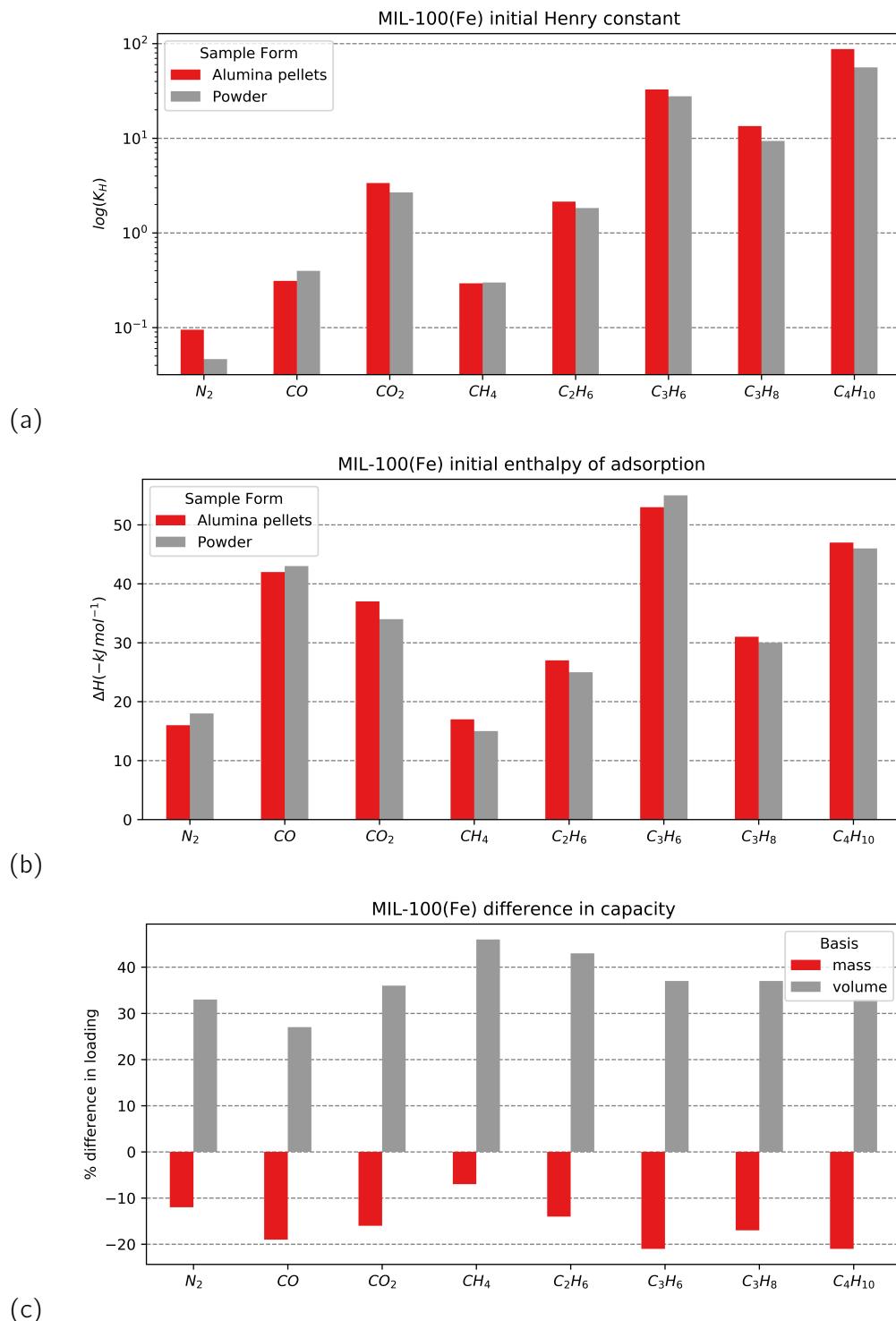
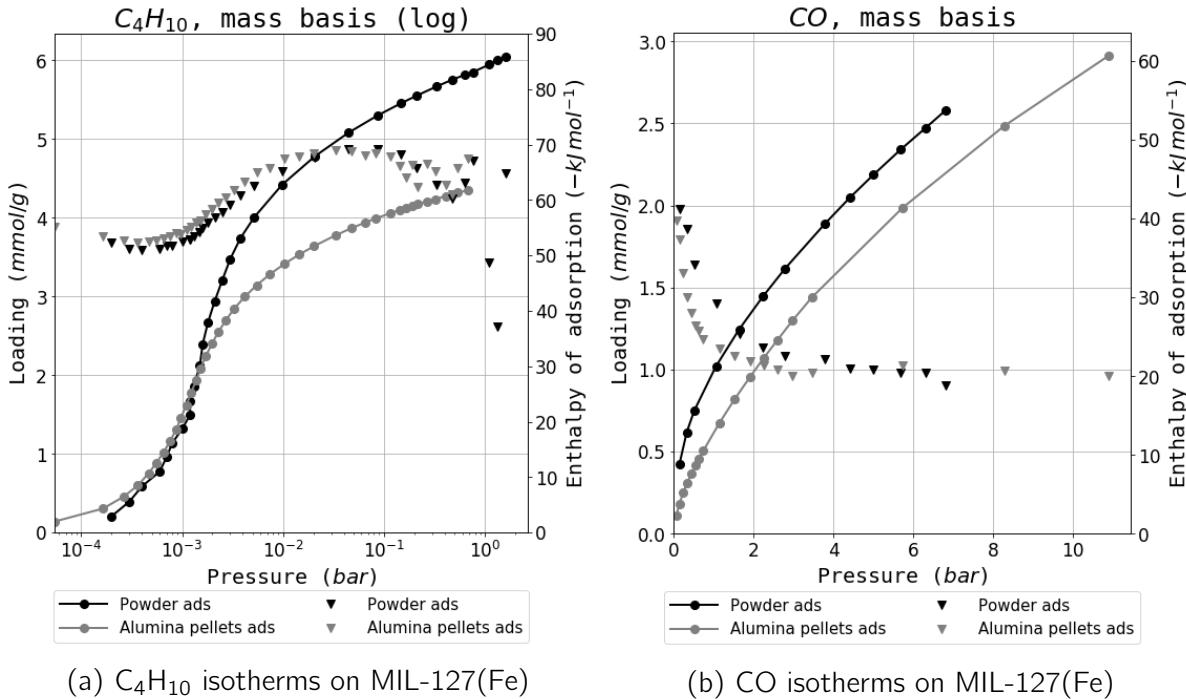


Figure 1.6: MIL-100(Fe) analysis

isotherm. As for the underlying reason behind the isotherm divergence, it could be that the alumina binder acts as a protector against the generation of iron(II) during thermal activation. No other differences are seen between the two forms on either Henry constant and initial enthalpy of adsorption.



The capacity comparison in Figure 1.8c paints an interesting picture. For most probes there is no change in maximum loading showing that there is no structure degradation or pore filling. Two outliers are apparent: carbon monoxide and butane. The decrease in capacity on CO can be explained through the aforementioned changes in active site prevalence. The drop in butane cannot be a consequence of the same effect as there is a perfect overlap in the enthalpy curves. Therefore it best explained through a size exclusion effect as seen on UiO-66(Zr).

Overall, MIL-127(Fe) shows excellent performance when undergoing alumina shaping, with almost no capacity loss, as long as the adsorbent is not carbon monoxide or butane, where specific effects come into play.

## 1.5 Conclusion

It can be concluded that the process of alumina shaping does not, in general, have an impact on the surface chemistry of the three MOF materials. Interestingly, in regards to the changes in maximum capacity, each material has its own particular behaviour: UiO-66(Zr) has a higher loss in capacity with larger molecular probes, MIL-100(Fe) has a decrease of 10-20% across all gasses and MIL-127(Fe) matches loading on a mass basis except on CO and C<sub>4</sub>H<sub>10</sub>.

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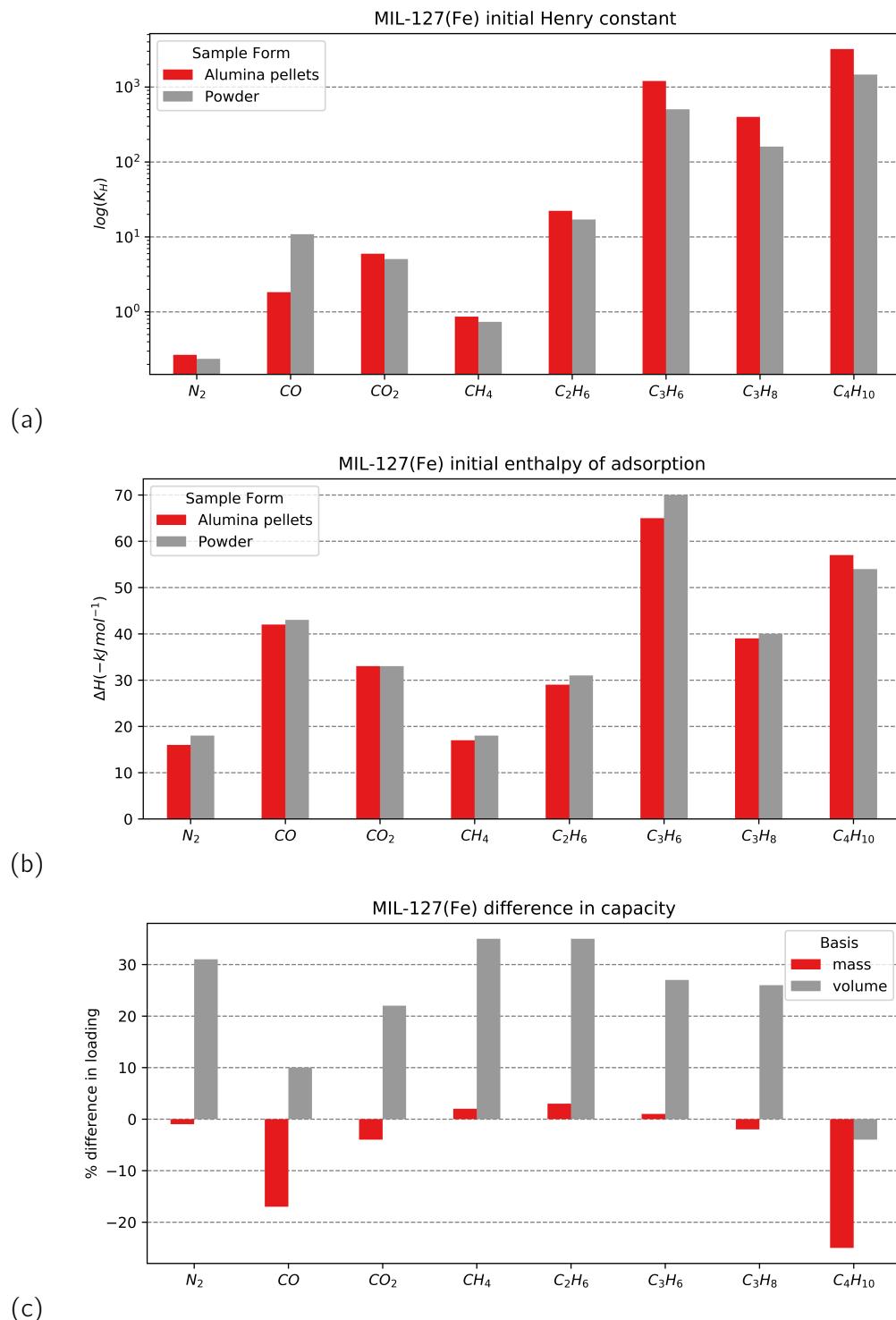


Figure 1.8: MIL-127(Fe) analysis

## *1 Exploring the impact of material form on adsorption measurements*

The shaping also induces a densification which, in almost all cases, leads to a better performance on a volumetric basis. However, the influence on the mass transport effects of the alumina binder is not known and should be investigated further.

Overall, the process of alumina shaping is a promising method of preparing MOFs for gas-related applications in separation and storage, but care should be taken to not generalise the effects present on one material to another.

# Common characterisation techniques

## 1 Thermogravimetry

TGA experiments were carried out on ca. 15 mg sample with a Q500 (TA Instruments) apparatus in a dynamic “Hi-Res” mode using  $3\text{ K min}^{-1}$  under both nitrogen and argon flow at  $30\text{ cm}^3 \text{ min}^{-1}$ . For comparison, the curves have been normalized at  $800\text{ }^\circ\text{C}$ .

## 2 Bulk density determination

Bulk density was determined by weighing 1.5 ml empty vessels and settling the powder or the spheres of the MOFs inside. Powders have been added by small increments and settled through vibration between each addition. We finally weighed the full vessels, which allowed the bulk density to be determined. The experiments were recorded with the same vessel after cleaning.

## 3 Nitrogen physisorption at 77 K

Nitrogen physisorption at 77 K was used to calculate BET areas and accessible pore volumes.<sup>(24)</sup> Approximately 60 mg of sample were used for each measurement. The adsorption experiments were carried out on a Micromeritics Triflex apparatus. The BET area on these microporous solids was calculated using the procedure devised by [Rouquerol et al.](#) Accessible pore volume was calculated from the amount adsorbed at  $p/p^0 = 0.2$ . The pore sizes were calculated by applying the Dollimore-Heal method on the desorption branch of the isotherm.

## 4 Vapour adsorption

Adsorption of water or ethanol vapour was measured at 298 K on a BELmax apparatus (MicrotracBEL, Japan). Approximately 50 mg of material was used for each experiment.

# Synthesis method of referenced materials

## 1 UiO-66(Zr) for shaping study

## 2 MIL-100(Fe) for shaping study

## 3 MIL-127(Fe) for shaping study

MIL-127(Fe) was synthesized by reaction of  $\text{Fe}(\text{ClO}_4)_3 \cdot 6 \text{H}_2\text{O}$  (3.27 g, 9.2 mmol) and  $\text{C}_{16}\text{N}_2\text{O}_8\text{H}_6$  (3.3 g) in DMF (415 ml) and hydrofluoric acid (5 M, 2.7 ml) at 423 K in a Teflon flask. The obtained orange crystals were placed in DMF (100 ml) and stirred at ambient temperature for 5 h. The final product was kept at 375 K overnight. MIL-127(Fe) was synthesized by reaction of  $\text{Fe}(\text{ClO}_4)_3 \cdot 6 \text{H}_2\text{O}$  (3.27 g, 9.2 mmol) and  $\text{C}_{16}\text{N}_2\text{O}_8\text{H}_6$  (3.3 g) in DMF (415 ml) and hydrofluoric acid (5 M, 2.7 ml) at 423 K in a Teflon flask. The obtained orange crystals were placed in DMF (100 ml) and stirred at ambient temperature for 5 h. The final product was kept at 375 K overnight.

# Complete adsorption dataset for shaping study

## 1 Calorimetry dataset UiO-66(Zr)

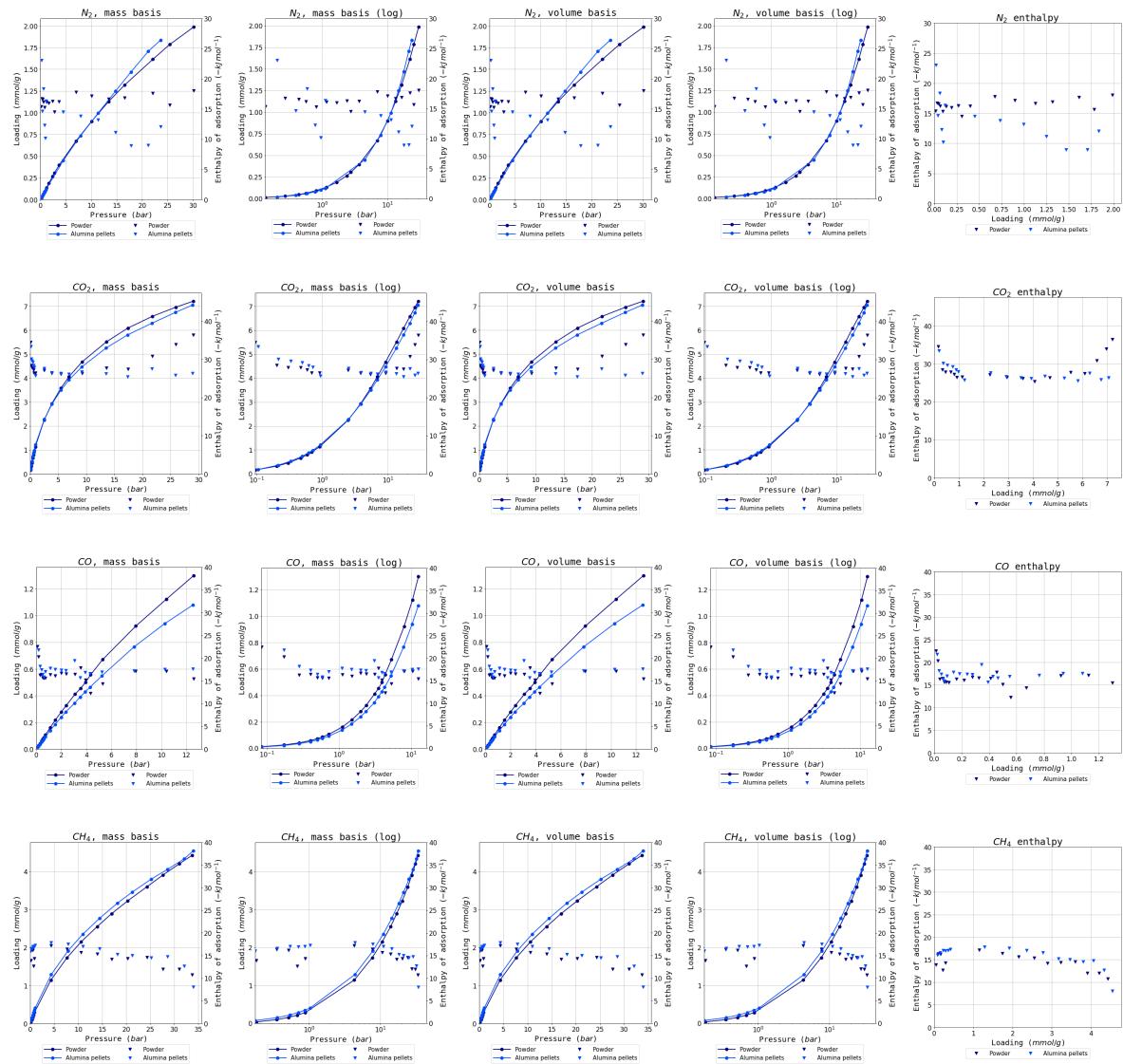


Figure 1: Complete isotherm and enthalpy dataset for  $UiO-66(Zr)$

# Complete adsorption dataset for shaping study

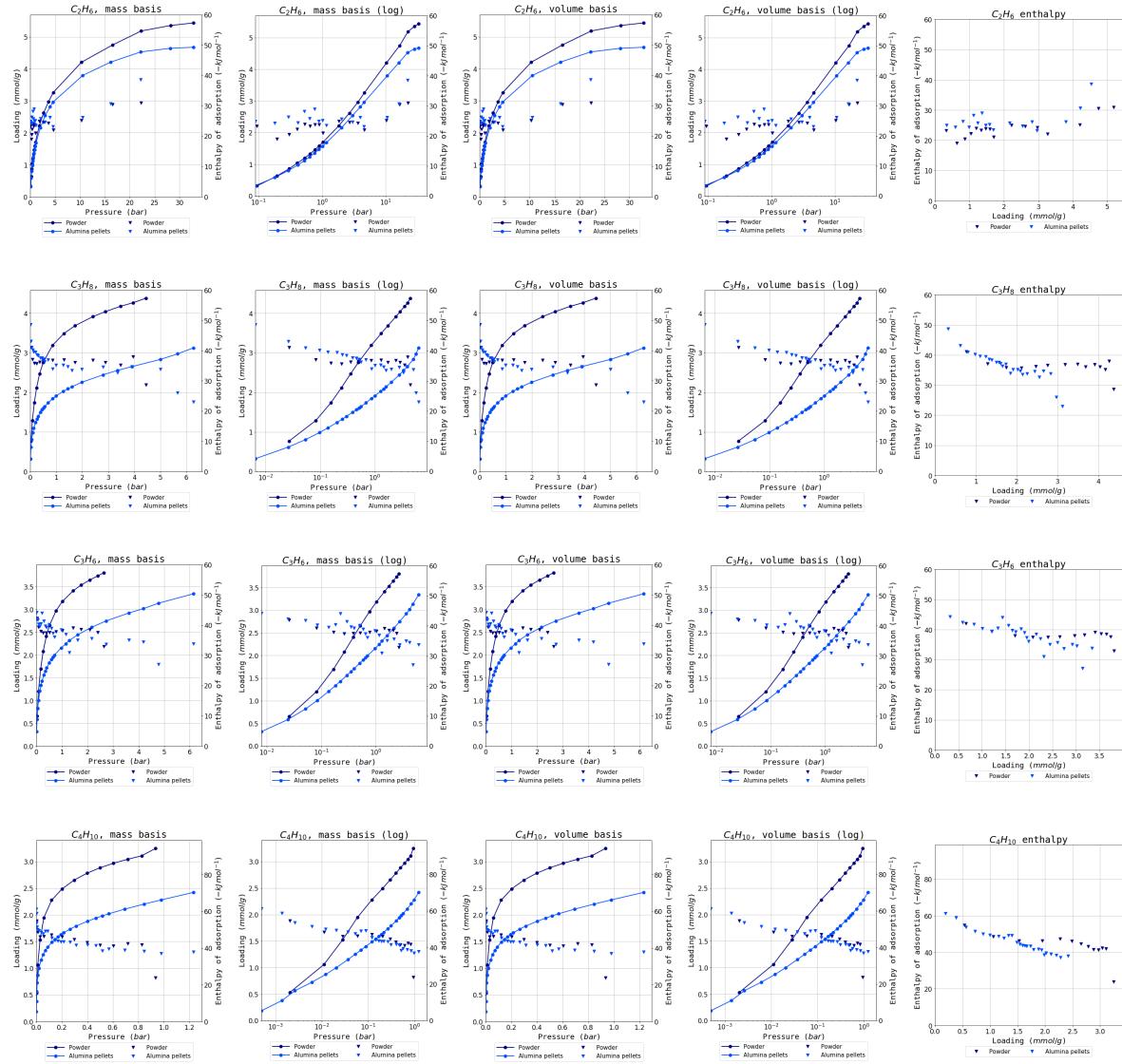


Figure 1: Complete isotherm and enthalpy dataset for  $\text{UiO-66}(\text{Zr})$

## 2 Calorimetry MIL-100(Fe)

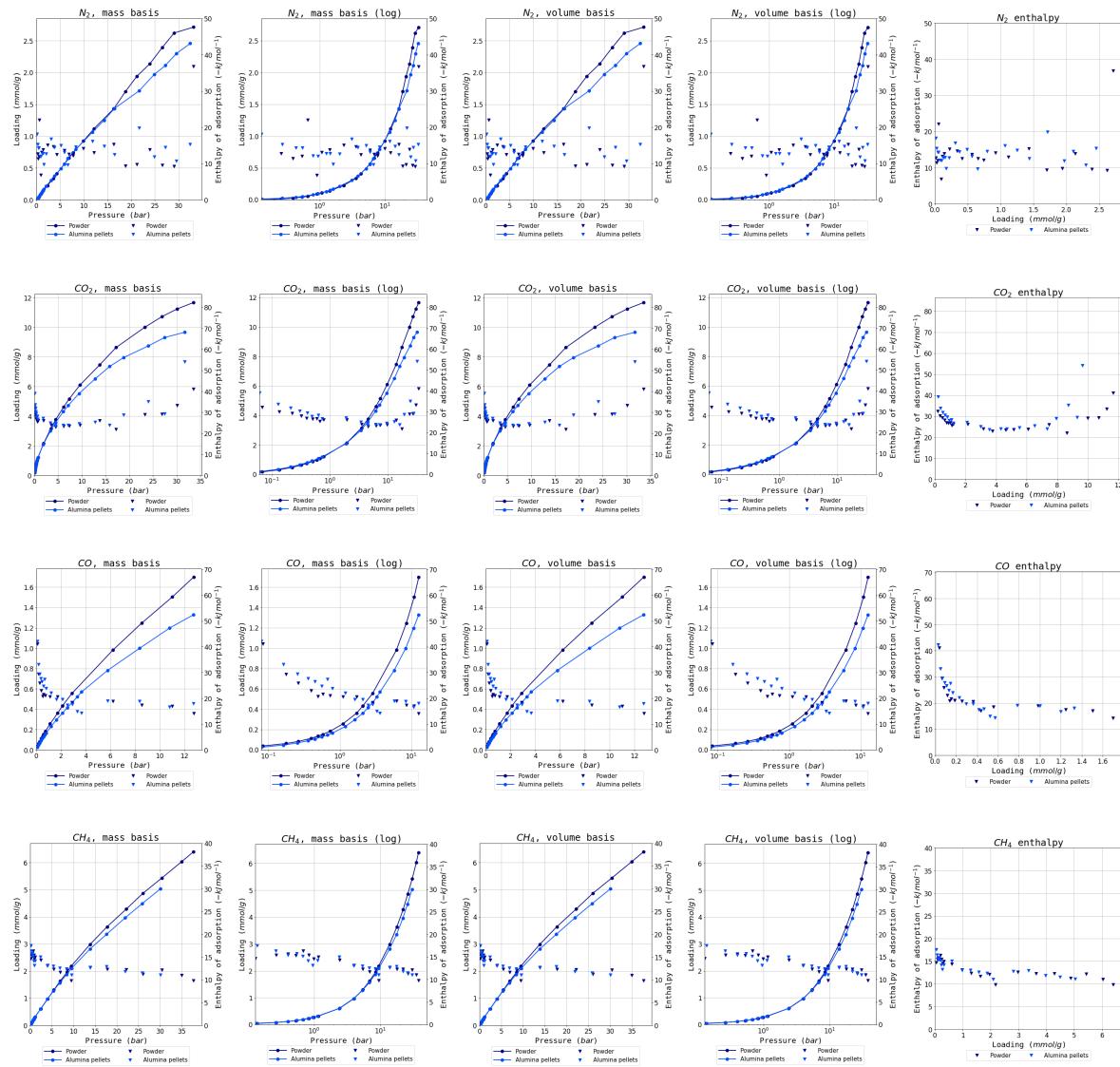


Figure 2: Complete isotherm and enthalpy dataset for MIL-100(Fe)

## Complete adsorption dataset for shaping study

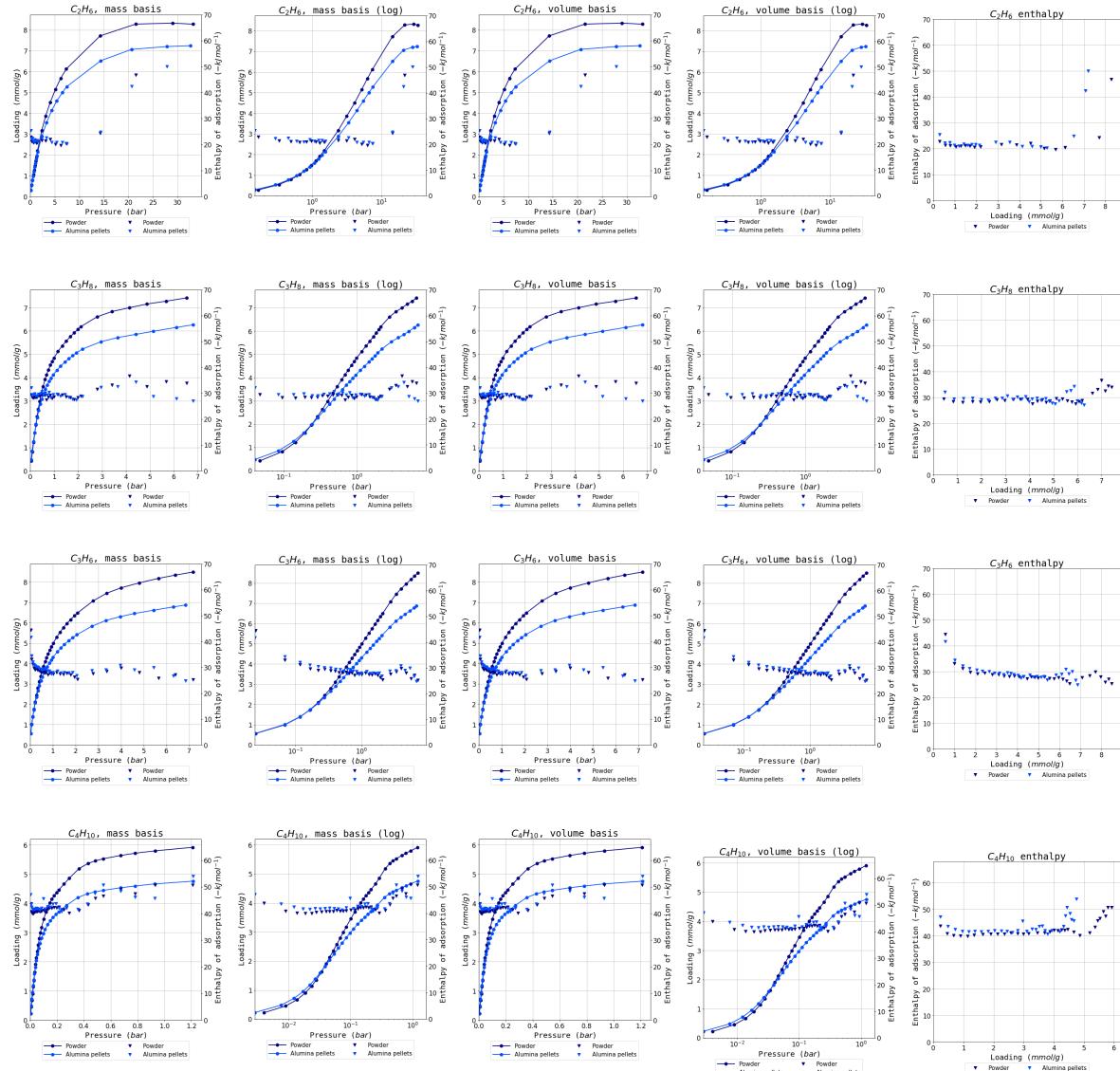


Figure 2: Complete isotherm and enthalpy dataset for MIL-100(Fe)

### 3 Calorimetry MIL-127(Fe)

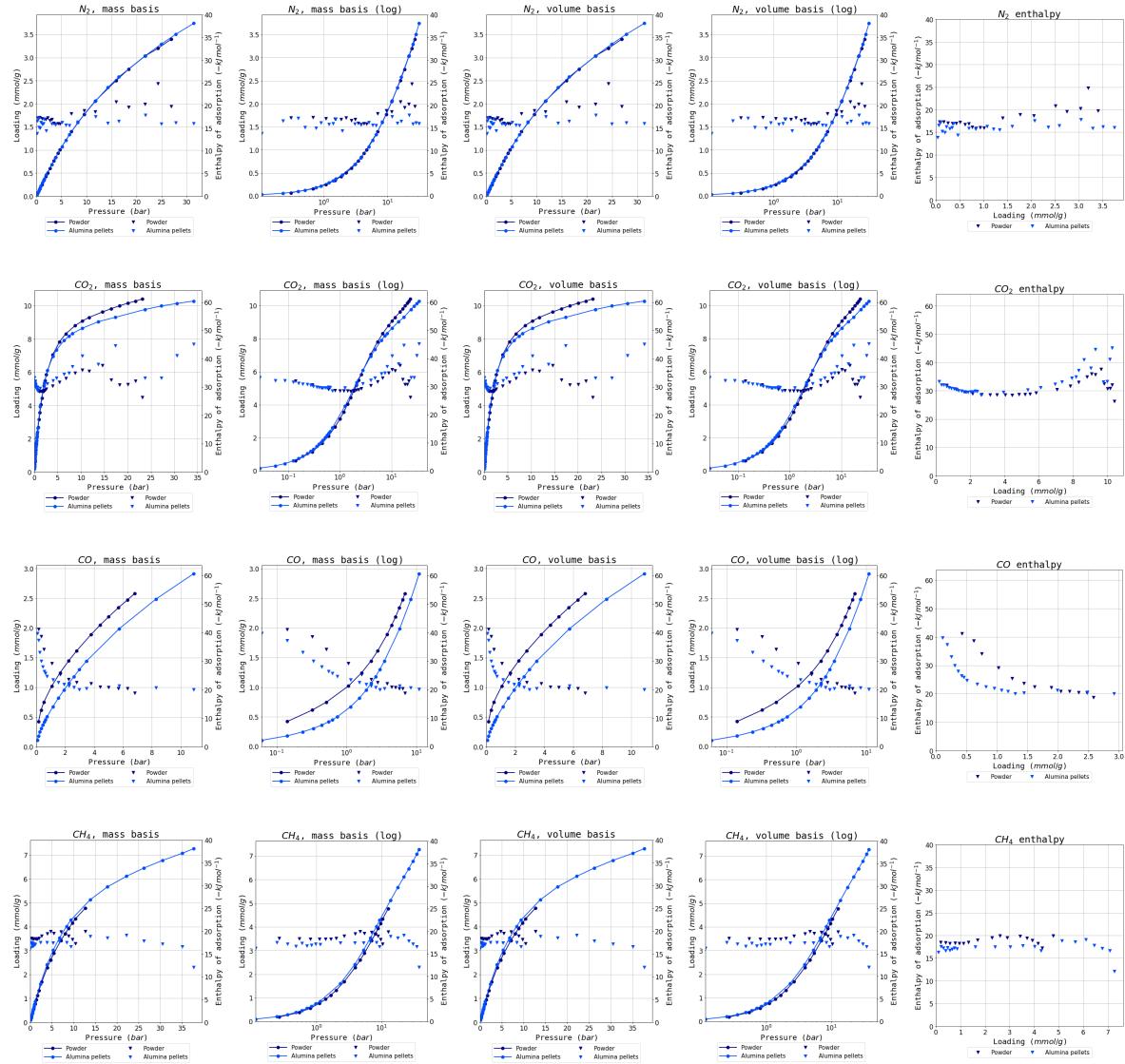


Figure 3: Complete isotherm and enthalpy dataset for MIL-127(Fe)

## Complete adsorption dataset for shaping study

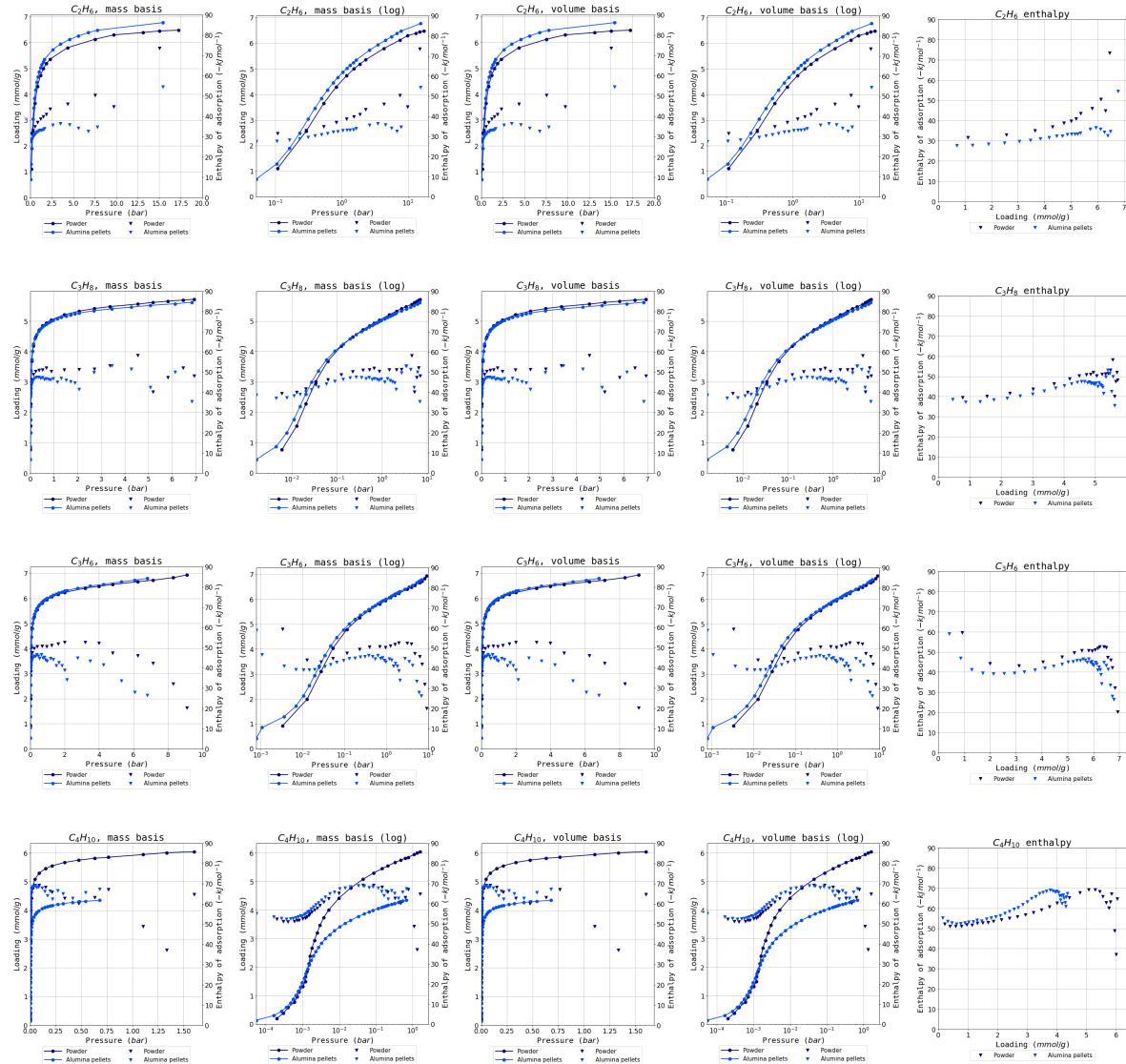


Figure 3: Complete isotherm and enthalpy dataset for MIL-127(Fe)

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