In this contribution, we present an extensive investigation of adsorption of a range of different gases at various temperatures in DUT-49, a metal-organic framework which features a negative gas adsorption (NGA) transition. Adsorption experiments at temperatures ranging from 21 to 308 K, were used to identify, for each guest, a critical temperature range in which NGA occurs. The experimental results were complemented by molecular simulations that rationalize the absence of NGA at elevated temperatures and the non-monotonic behavior observed upon temperature decrease.
The Role of Temperature and Adsorbate on Negative Gas Adsorption in the Mesoporous Metal-Organic Framework DUT-49

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Abstract

Unusual adsorption phenomena, such as breathing and negative gas adsorption (NGA), are rare and challenge our understanding of the thermodynamics of adsorption in deformable porous solids. In particular, NGA appears to break the rules of thermodynamics by exhibiting a spontaneous release of gas accompanying an increase in pressure. This apparent anomaly is in fact due to long-lived metastable states, and a fundamental understanding of this process is required for the discovery of new materials with this exotic property. Interestingly, NGA was initially observed upon adsorption of methane in the metal-organic framework DUT-49 at relatively low temperature, close to the respective standard boiling point of the adsorptive, and no NGA was observed in the same host/guest system at higher temperatures. In this contribution, we present an extensive investigation of adsorption of a range of different gases at various temperatures in DUT-49, a material which features an NGA transition. Experiments at temperatures ranging from 21 to 308 K, were used to identify, for each guest, a critical temperature range in which NGA occurs. The experimental results were complemented by molecular simulations that rationalize the absence of NGA at elevated temperatures and the non-monotonic behavior observed upon temperature decrease. Furthermore, this in-depth analysis highlights the crucial thermodynamic and kinetic conditions for NGA that is unique to each guest and potentially other solids with...
similar effects. We expect this exploration to provide detailed guidelines for experimentally
discovering NGA and related “rule breaking” phenomena in novel and already reported materials,
and furthermore, specify conditions required for the practical application of this effect, for
example as pressure amplifying materials.

Introduction
Structural flexibility and softness in porous crystals has generated new adsorption phenomena
beyond the classified types of isotherms known for rigid adsorbents. While gradual swelling of
soft porous solids upon adsorption of fluids has been known for decades, cooperative well-
deﬁned structural transformations in soft porous crystals have led to predeﬁned adsorption
behavior, governed by reversible crystal-to-crystal structural transformations. Especially in the
field of metal-organic frameworks (MOFs), adsorption-induced ﬂexibility frequently gives rise to
stepwise isotherms governed by single or multiple steps and wide hysteresis dictated by expansion
or contraction of the pores. Due to their uncommon adsorption behavior, these materials are
being discussed as alternative adsorbents in the area of gas sensing, storage or separation.
In early examples of adsorption-induced transitions in MOFs, it was shown that the pores in a
condensed framework can be expanded upon application of gas pressure. In this phenomenon,
called gate-opening, the adsorbate stabilizes the presence of the open pores (op), which
subsequently collapses upon reduction in gas pressure and subsequent desorption of the gas
molecules from the pores. However, attractive solid-ﬂuid and ﬂuid-ﬂuid interactions can also
result in large-scale contraction of the pores upon adsorption. This was ﬁrst demonstrated in the
MIL-53(Al) in which the open pore (op) channels are found to undergo contraction upon
adsorption of gases at intermediate pressure. Accompanying a further increase in gas pressure,
the contracted pores (cp) are reopened to the initial op structure via structural expansion, and
these successive transitions in MIL-53 where thus referred to as breathing. In both gate-opening
and breathing materials, the experimentally observable isotherms represent a mixture of the
single component isotherm of each structural phase with transition regions, which represent a
mixture present in the corresponding pressure range. The step-wise isotherms, and switching of
the solid, is caused by highly inelastic transformations due to an anharmonic Helmholtz free
energy profile upon deformation (F(𝑋), where 𝑋 represents a deformation). In recent years,
several computational studies have demonstrated that adsorption-induced structural transitions
stem from a complex interplay between the structural ﬂexibility of the MOF and the solid-ﬂuid and
fluid-ﬂuid interactions. Beyond the nature of the solid and ﬂuid, temperature effects were
found to have a large impact on the presence of breathing, observed in the systems MIL-53\textsuperscript{19, 20} and ZIF-8\textsuperscript{21}, however little experimental and computational work has been performed beyond these systems.

In 2016, we discovered the phenomenon of negative gas adsorption (NGA), initially observed in the MOF DUT-49\textsuperscript{22} (Dresden University of Technology No. 49), which is characterized by a negative step in the adsorption isotherm originating from adsorption-induced structural contraction of the pores\textsuperscript{23}. This adsorption behavior is unique for both rigid and flexible adsorbents, although large-scale adsorption induced-structural contraction is known to occur in other solids, such as MIL-53.

Computational analysis has revealed that the formation of a metastable adsorption state is a prerequisite for NGA\textsuperscript{24}. The \textit{op-cp} transition is energetically driven by an increase in adsorption interactions in the reduced pore volume, well reflected by an increase in adsorption enthalpy upon contraction, which was investigated both experimentally and computationally\textsuperscript{25}. The excess amount of adsorbate present in the pores of the \textit{op} state before contraction ($n_{op}$) and excess of the amount of adsorbate present in the \textit{cp} phase after contraction ($n_{cp}$) defines the amount of gas released upon NGA, further termed $\Delta n_{NGA}$. (1)

$$\Delta n_{NGA} = n_{op} - n_{cp}$$ (1)

The structural contraction strongly depends on the softness of the framework and we recently found that shortening of the ligand backbone increases stability and consequently prevents NGA. While elongation increases softness, resulting in the discovery of the second NGA material, DUT-50\textsuperscript{26}. Although this study demonstrated a design principle for the synthesis of other materials capable of NGA, the initial discovery and experimental adsorption conditions used in previous studies, such as methane adsorption at 111 K, were very much serendipitous. These conditions were originally chosen for instrumental reasons, to be able to record the full relative pressure range below ambient pressure and avoid the application of high pressure. Interestingly, the occurrence of NGA upon adsorption of other gases, such as $n$-butane (298 K)\textsuperscript{23}, nitrogen (77 K)\textsuperscript{27}, and xenon (200 K),\textsuperscript{28, 29} was observed at temperatures close to the respective standard boiling point of the adsorptive while no structural contraction, or NGA, was found at elevated temperatures and pressures (methane 298 K, xenon 273 K). In addition, structural contraction without the presence of NGA (breathing behavior, similar to adsorption behavior of MIL-53\textsuperscript{19, 20}) is observed upon adsorption at reduced temperatures for some gases ($n$-butane at 273 K, xenon at 165 K). Consequently, three distinct adsorption trajectories have been identified for DUT-49:
structural contraction without NGA, structural contraction with NGA, and no adsorption-induced structural contraction (Fig. 1).

Fig. 1. Adsorption isotherms of DUT-49 upon a) structural contraction without NGA, b) structural contraction with NGA, and c) no structural transition (grey area indicates presence of cp phase), d) crystal structure of DUT-49op and e) corresponding pore size distribution, g) crystal structure of DUT-49cp and f) corresponding pore size distribution. Cuboctahedral pore green, tetrahedral pore blue, octahedral pore orange.

NGA was observed for the adsorption of methane in an extended temperature range of 91-121 K\textsuperscript{23}. However, within this temperature window, the values for $\Delta n_{\text{NGA}}$ were found to vary non-monotonically and similar behavior was observed upon adsorption of $n$-butane (273-303 K) and xenon (195-273 K). Guest-free DUT-49op was found to exhibit elastic negative thermal expansion, not a step-wise transition, in the range of 77-600 K using variable temperature powder X-ray diffraction (PXRD)\textsuperscript{23}. Computational analysis of the structural transition supports these findings, showing that entropic and temperature effects in the solid phase have negligible contribution to structural contraction and NGA\textsuperscript{24}. Structural contraction upon adsorption of methane, investigated by in situ PXRD, was found to yield identical cp phases in the temperature range of 91-120 K, demonstrating that $\Delta n_{\text{NGA}}$ is not a function of variation in structural contraction.\textsuperscript{23} Consequently, the origin of variation in NGA-behavior is expected to originate from the temperature-dependent solid-fluid and fluid-fluid interactions. Hence, we raise the question: beyond the generic structural
contraction, which adsorption conditions are required to obtain NGA and maximize $\Delta n_{NGA}$ in DUT-49?

In this contribution, we analyze the presence of NGA in DUT-49 experimentally by adsorption experiments with 14 different gases, and vapors, covering a temperature range of 21-308 K. We derive, from these experiments, an empirical correlation between the critical temperature of the fluid, the presence of NGA, and its magnitude, defined by $\Delta n_{NGA}$. Furthermore, we rationalize the observed high and low temperature limits of NGA by molecular simulations and define criteria that might lead to the discovery of NGA in other flexible, and previously thought non-flexible, porous solids.

**Adsorption experiments**

To ensure that the adsorption behavior is free of sample effects, such as particle size and defects which are known to impact NGA in DUT-49, a large batch of DUT-49 was synthesized and activated according to the previously published procedure. All experiments described in this work were conducted on samples from this particular batch. Using a home-built high pressure adsorption cell, connected to a helium closed-cycle cryostat system and commercial adsorption instrumentation, we are able to record adsorption/desorption isotherms with high accuracy in the temperature and pressure range of 21-308 K and 0.001-30 MPa, respectively (see Supplementary material section 2 for details). Beginning from the initial dataset of methane in the range of 91-121 K, we repeated, and extended, the temperature range by recording isotherms in the range of 91-190 K in steps of 10 K. Attempts to record methane adsorption isotherms at temperatures lower than 91 K were experimentally unfeasible, due to condensation or crystallization of bulk methane in the instrument and sample cell which prevent adequate equilibration. Interestingly, structural contraction (evidenced by hysteresis at intermediate pressures) and NGA are only observed in the temperature range of 91 to 130 K. From this adsorption data, we established a phase diagram for the presence of the $op$ and $cp$ phase of DUT-49 upon adsorption of methane (Fig. 2b). When compared to the phase diagram of methane adsorption in MIL-53, one of the few flexible MOFs known to undergo breathing transitions, the $T$-$p$ range in which the $cp$ phase is present is strongly reduced for DUT-49. This can be explained by the smaller pore size of the channels in MIL-53 that are expected to exhibit strong confinement-induced solid-fluid interactions, even at elevated adsorption temperatures. Nevertheless, the shape and $p$-$T$ range, where structural contraction occurs, are similar for both materials with the exception that a small
range at the lower edge of the phase diagram shows the presence of NGA in DUT-49, not observed for MIL-53 so far.

Fig. 2. a) $\Delta n_{\text{NGA}}$ evolution upon adsorption of methane in DUT-49, presence of adsorption-induced structural contraction in blue, absence of contraction in red. b) experimental temperature-pressure dependent presence of DUT-49cp (green) in the area between contraction (open symbols) and reopening (closed symbols) with presence of metastable NGA region in blue upon adsorption of methane. Error bars correspond to the maximum resolution obtained from the isotherms. c-d) Adsorption (closed circles) and desorption (open circles) isotherms of methane in DUT-49 at 111 K (c) and 130 K (d), simulated adsorption isotherm of DUT-49cp given as orange line.

As previously observed, $\Delta n_{\text{NGA}}$ values extracted from the isotherms in the range of 91-130 K show as a function of temperature a non-monotonic trend, with a maximum of 6.15 mmol g$^{-1}$ at 100 K. Upon increasing temperature, the hysteresis width at intermediate pressure, which corresponds to the $cp$ to $op$ transition, shrinks (Fig. 2 c,d, Supplementary Figure 3) and the plateau corresponding to adsorption in the $cp$ phase exhibits higher uptake than expected for DUT-49cp (Fig. 2 c,d). This behavior can either be assigned to the formation of intermediate phases ($ip$) or incomplete contraction of the bulk $op$ phase. Both scenarios were previously observed with adsorption of nitrogen at 77 K in DUT-49 samples with reduced crystal size$^{27}$. Desorption isotherms in the range of 91-135 K exhibit an inverse hysteresis around the NGA step in which the desorption branch undercuts the adsorption branch (Fig. 2 c,d). This indicates a structural contraction following isothermal desorption from the pores. In the temperature range of 140-190 K no hysteresis was observed indicating an absence of structural transitions (Supplementary Figure 3). Consequently, recovery of guest free DUT-49op after NGA could be achieved by increasing the temperature at a pressure beyond 300 kPa, beyond 160 K, and subsequently removing the methane in vacuum. This allows for cycling NGA by subsequently performing adsorption at reduced temperatures in the range of 91-130 K.
To investigate whether the non-monotonic evolution of $\Delta n_{\text{NGA}}$ as a function of temperature is universal, the study of methane adsorption was first extended by analysing a series of hydrocarbons and hydrogen at or below their respective standard boiling points (Supplementary Figure 1). Among the adsorptive/temperature combinations tested, hydrogen is the only adsorptive to neither show contraction nor NGA. Methane (111 K) and ethene (169 K) exhibit NGA while the rest of the series exhibit contraction and hysteresis without the presence of NGA. As previously observed for $n$-butane,$^{23}$ NGA was found to occur with increasing adsorption temperature. Thus, isotherms at temperatures above the boiling point were recorded for ethene, ethane, propane, and $n$-butane. Increasing temperature, from 169 to 199 K, $\Delta n_{\text{NGA}}$ increases from 1.23 to 8.08 mmol g$^{-1}$ for the adsorption of ethene (Supplementary Figure 4) and the $\Delta n_{\text{NGA}}$ value recorded at 199 K is the highest observed for all hydrocarbons investigated in this study. NGA is observed for the adsorption of ethane in the range of 200 to 240 K, and $\Delta n_{\text{NGA}}$ reaches a maximum of 4.03 mmol g$^{-1}$ at 220 K. No NGA occurs above 220 K and in the range of 184 to 220 K structural contraction without NGA is observed (Supplementary Figure 5). NGA at 230 and 240 K occurs at 132 and 216 kPa, which represents pressure amplification well above ambient pressure that is required for air bag-type or pneumatic applications. The series of experiments was further extended by adsorption of propane in the temperature range of 231 to 298 K (Supplementary Figure 6). At these investigated temperatures, NGA is only observed at 261 K, with a respective $\Delta n_{\text{NGA}}$ value of 1.77 mmol g$^{-1}$, and no contraction is observed at 298 K. The shape of the adsorption branch indicates that structural contraction occurs at all temperatures except at 298 K, however without NGA. To further characterize the nature of the structural transition we employed in situ PXRD upon adsorption of propane at 231 K (Supplementary Figure 17) and ethane at 185 K (Supplementary Figure 18). In comparison to the structural contraction following methane adsorption at 111 K and $n$-butane at 298 K, which was previously analysed$^{23}$, a similar cp formation is observed for ethane and propane (Supplementary Figure 19). However, severe peak broadening and the presence of an additional peak at lower diffraction angles, for cp formation upon propane adsorption, indicate the formation of a more disordered state, which might explain the difference in adsorption behaviour compared to other hydrocarbons. Nevertheless, in all other cases DUT-49 responds in a comparable fashion allowing the direct comparison of the isotherms and NGA transitions. Including the previously published adsorption data of $n$-butane in the range of 273-308 K$^{23}$ an interesting trend can be observed: For each gas a non-monotonic evolution of $\Delta n_{\text{NGA}}$ with temperature is observed (Fig. 3).
Fig. 3.  a) $\Delta n_{\text{NGA}}$ correlating with adsorption temperature $T$ for a series of hydrocarbons and noble gases, b) correlation of critical temperature, $T_c$, with temperatures at which NGA is observed, $T_{\text{NGA}}$. Linear fits for $T_{\text{NGA}}$ (red dashed line) and highest experimentally observed temperature at which NGA occurs referred to as maximum $T_{\text{NGA}}$ (black line).

As described above, for each gas a low temperature limit is observed for which DUT-49 is found to contract with an absence of NGA, referred to as $T_{\text{low}}$ (the minimal $T$ for which $\Delta n_{\text{NGA}} > 0$). With increasing temperature $\Delta n_{\text{NGA}}$ is found to increase, reaching a maximum at a temperature, $T_{\text{NGA}}$. Following a further increase in temperature, a decrease in $\Delta n_{\text{NGA}}$ is observed and an increase in uptake in the plateau after structural contraction is observed, which was previously assigned to incomplete structural contraction of the bulk sample demonstrated by in situ PXRD\textsuperscript{27}. At a certain upper temperature limit, referred to as $T_{\text{high}}$ (the maximum $T$ for which $\Delta n_{\text{NGA}} > 0$), no structural contraction and reversible adsorption/desorption behaviour is observed. In the following, we thus define the temperature $T = T_{\text{NGA}}$ at which $\Delta n_{\text{NGA}}$ reaches a maximum for a given adsorbate, $T = T_{\text{low}}$ for the low temperature limit of NGA, $T = T_{\text{high}}$ for the high temperature limit of NGA and $T_{\text{high}} - T_{\text{low}}$ thus defines the range where NGA is observed for a respective adsorptive. Although all gases are hydrocarbon-based, their increase in chain length suggests that the observed behaviour is of more general nature and not a factor of chemical composition. In fact, the same evolution of $\Delta n_{\text{NGA}}$ was previously found upon adsorption of xenon used as a probe molecule for in situ NMR experiments\textsuperscript{28, 29}. To test whether this observation is supported for other noble gases, a series of adsorption experiments were conducted using argon and krypton in the temperature range of 77-110 K and 120-160 K, respectively. A comparable temperature dependent evolution of $\Delta n_{\text{NGA}}$ is obtained for both gases with argon reaching a maximum of 10.5 mmol g\textsuperscript{-1} at 95 K and krypton 6.3 mmol g\textsuperscript{-1} at 140 K. Interestingly, no NGA and structural contraction where observed upon adsorption of argon at 105 K, however structural contraction and inversed hysteresis were observed upon desorption in the low pressure range. This indicates that the activation barrier for
adsorption-induced contraction is lower upon desorption compared to the adsorption process and might provide further insight to the irreversible contraction upon desorption of other adsorbates. Most importantly, the experiments conducted demonstrate that NGA in DUT-49 can be obtained in the a wide temperature range of 77-310 K by selecting the appropriate adsorbate. This is an important fundamental observation and might also be relevant for the utilization of NGA for practical applications in pneumatic devices or others. However, the experiments also raise two fundamental questions: first, is there a generalizable correlation for a family of adsorbates that enables prediction of the temperature range where there is presence of $\Delta n_{\text{NGA}}$, and secondly, what properties govern this observed temperature dependence of NGA?

**Empirical correlation of $T_C$ with $T_{\text{NGA}}$**

In cylindrical mesoporous solids semi-empirical correlation of the pore critical temperature and the melting point depression with the critical temperature of the fluid are found for a variety of different pore sizes. Shrinkage and disappearance of the hysteresis loop at the hysteresis critical temperature reflects the temperature dependence of capillary condensation known to be related to NGA in DUT-49. To probe the presence of a correlation, we plotted $T_{\text{high}}, T_{\text{low}}, T_{\text{NGA}}$, and the whole temperature range for which NGA is observed against physical properties of the applied gases, such as the standard boiling point the critical temperature and their ratio (Supplementary Figure 15). In fact, the temperature range in which NGA is observed for each guest shows a linear correlation with the critical temperature, $T_C$, of the fluid and is expressed in equation (2).

$$T_{\text{NGA}} = i \cdot T_C - j \quad (2)$$

in which the parameters $i$ and $j$ can be fitted to experimental data. This linear correlation is observed for the three different temperature $T_{\text{high}}, T_{\text{low}}, T_{\text{NGA}}$, as well as the whole temperature range for which NGA is observed (Fig. 4).
Parameters $i$ and $j$ were determined to be $i = 0.74$ and $j = -6.43$ K for $T_{\text{high}}$, and $i = 0.82$ and $j = -54.1$ K for $T_{\text{low}}$, thus setting the limits for $T_{\text{NGA}}$ that is fitted with parameters of 0.78 and -26.1 K, respectively. The similarity of the slopes $i$ demonstrate that the temperature range of NGA for these gases is governed by a universal correlation. The difference in $j$ parameter obtained for both fits shows the average deviation of around 20 K between $T_{\text{high}}$, $T_{\text{low}}$, and $T_{\text{NGA}}$. This variation is within the temperature steps of 10 K of the performed adsorption experiments and shows that the resolution of the experiments is high enough to detect NGA for other gases, not explored in this study. The correlation of $T_c$ with $T_{\text{NGA}}$ is particularly useful, as it can be used to predict the temperature range where NGA can be expected to occur, and peak, for other gases. Because structural contraction with the absence of NGA did occur at or below the standard boiling point for long chain hydrocarbons, we can use equation 2, and the derived parameters, to estimate $T_{\text{NGA}}$ for other adsorptives. For example, $n$-pentane with a critical temperature of 469.6 K is expected to show NGA at 340 K, $n$-hexane ($T_c = 507.6$ K) at 369 K and $n$-heptane ($T_c = 540.6$ K) at 394 K. Hydrogen, with a critical temperature of 33.1 K, is expected to show NGA at 8.5 K, a temperature, which is 13 K below the investigated temperature where no structural contraction was observed. Not only can equation 2 provide an estimate of the temperature region where NGA occurs but also the temperature range where $\Delta n_{\text{NGA}}$ reaches a maximum. This is demonstrated for the adsorption of C$_4$ hydrocarbons, $n$-butane, 1,3-butadiene, 2-methylpropane with $T_c$ of 425.2 K, 425.1 K, and 407.7 K, respectively, where $\Delta n_{\text{NGA}}$ for the adsorption of $n$-butane and 1,3-butadiene at 298 K is comparable at around 1.3 mmol g$^{-1}$ but over doubled for the adsorption of methylpropane. Although it is observed that $\Delta n_{\text{NGA}}$ decreases with increasing molar volume of the condensed fluid, at the given adsorption temperature and saturation pressure ($p/p_0 = 1$), which correlates in part with $T_c$, no direct correlation was found to estimate the magnitude of $\Delta n_{\text{NGA}}$ as a
function of temperature, based on the performed experiments. Total uptake of condensed fluid in
the pores of DUT-49 op and cp can be estimated at saturation using the pore volume of the
structures and the molar volume of the fluid, but the magnitude of $\Delta n_{\text{NGA}}$ is primarily dictated by
how much the op phase can be overloaded, beyond the intersection of the op/cp isotherms. This
point of structural transition not only correlates to a specific loading of fluid, it is also correlated to
a specific $p_{\text{NGA}}$, the absolute pressure at which NGA occurs. Because adsorption isotherms, as a
function of absolute pressure, are strongly impacted by the adsorption temperature, comparison
of the relative pressure obtained from division with the vapour pressure, $p_0$, at a given
temperature permits comparison of isotherms at different temperatures and at the same relative
pressure range. In all experiments performed, structural contraction and NGA were found to be in
the relative pressure region of 0.09 to 0.19, which correlates to the pressure range where
mesopore filling occurs, as previously analysed by in situ neutron diffraction$^{26}$. Accompanying
increasing $T$ and $\Delta n_{\text{NGA}}$ not only the absolute pressure of transition at which NGA occurs, $p_{\text{NGA}}$, but
also the relative transition pressure, $p_{\text{NGA}}/p_0$, is shifted to higher pressures. Similar to the
correlation between $T_c$ and $T_{\text{NGA}}$, the relative transition pressure $p_{\text{NGA}}/p_0$ was found to linearly
grow with the critical pressure $p_c$ of the fluid (Supplementary Figure 16). To estimate an empirical
correlation similar to the study of temperature dependence of $\Delta n_{\text{NGA}}$, values of $p_{\text{NGA}}/p_0$ were taken
at $T_{\text{NGA}}$ for the series of gases previously discussed. The upper temperature limit of NGA for some
gases has not been reached, because $\Delta n_{\text{NGA}}$ as a function of $T$ was analysed in 10 K steps. This is
expected to impact the accuracy of the pressure more drastically than for the previous correlation
with temperature. Thus, an error for $p_{\text{NGA}}/p_0$ was estimated based on the resolution of the
pressure range obtained from the conducted experiments. By using equation (3), $p_{\text{NGA}}$ can be
estimated for different gases using the vapor pressure $p_0$ as a function of $T_{\text{NGA}}$.

$$p_{\text{NGA}} = (l \cdot p_c) \cdot p_0$$  \hspace{1cm} (3)

Due to the relatively low number of adsorption experiments around the upper temperature limit,
the empirically estimated factor $l$ of 0.032 is expected to underestimate $p_{\text{NGA}}$. However, it does
provide an estimation of the transition pressure at which contraction and NGA are to be expected,
and thus present another tool of narrowing the conditions where NGA transitions are expected for
a given adsorptive in DUT-49.

Canonical ensemble for determination of high temperature limit ($T_{\text{high}}$)

Although the empirical correlations above provide guidelines for the discovery of NGA transitions
in DUT-49 in defined temperature and pressure ranges, we sought to provide an analysis of the
fundamental thermodynamic and kinetic aspects responsible for the non-linear evolution of $\Delta n_{\text{NGA}}$
with temperature. As described in eq. 1, NGA is based on an interplay between the adsorption
properties of the \textit{op} and \textit{cp} phase in DUT-49. As the metastable region in the isotherm that represents the NGA transition is difficult to capture using existing experimental and computational techniques, as a first approximation we consider the presence of adsorption-induced structural contraction as a prerequisite for NGA to occur. Coudert \textit{et al.} were previously successful in simulating the $p,T$ phase-diagram of methane adsorption in MIL-53 using the osmotic ensemble, $\Delta \Omega_{OS}(T,p)$, as a function of adsorption temperature, $T$, and pressure, $p$, the free energy difference between the open and contracted state, $F_{op-cp}$, and change in volume, $V_{op-cp}$, the adsorbed amount, $n_{ads}$, as well as the molar fluid volume $V_m$, described in equation (4).

$$\Delta \Omega_{OS}(T,p) = \Delta F_{op-cp} + p \Delta V_{op-cp} - \int_0^p n_{ads}(T,p)V_m(T,p)dp$$ (4)

Although a detailed analysis of structural transition for DUT-49 has been performed\textsuperscript{24}, the temperature dependence of the adsorption energetics have not been fully characterized yet. To analyze the adsorption-induced structural transition upon adsorption of methane in DUT-49, we thus simulated a series of isotherms for the \textit{op} and \textit{cp} phase in the temperature range of 91-190 K with 10 K increments using grand canonical Monte Carlo (GCMC) simulations, i.e. with rigid description of the host material for each phase. These simulations complement the previously discussed experimentally recorded isotherms. In general, we find good agreement between the simulated and experimental adsorption isotherms and capture the intersection of the isotherms of both phases with high accuracy validating the computational analysis and derived adsorption energetics. As primary condition for the occurrence of NGA, we take the structural contraction of the \textit{op} phase beyond the crossing point of the \textit{op} and \textit{cp} isotherms: this crossing point corresponds to an adsorbed amount $n_{op-cp}$ and pressure $p_{op-cp}$. From the simulated isotherms these values can easily be defined and $\Delta f_i$ can now be expressed as a function of $\Delta n_{NGA}$ using Equation 5:

$$\Delta f_i = \Delta \Omega_{OS} - \Delta F_{op-cp}$$ (5)
Fig. 5 a) GCMC simulations of methane adsorption for the \( op \) (solid lines) and \( cp \) phases (dashed lines) of DUT-49 with intersection (\( n_{op} = n_{cp} \)) marked as circles. b) \( \Delta_i \) as a function of \( n_{op} - n_{cp} = \Delta n_{NGA} \) with 900 kJ mol\(^{-1}\) indicated by a horizontal line as transition energy and 0 \( \Delta n_{NGA} \) indicated as a vertical dashed line.

The difference in osmotic potential not only can characterize the energetic conditions for temperature dependent adsorption-induced contraction in DUT-49, but it can also indicate the free energy difference upon contraction as a function of \( \Delta n_{NGA} \), thus defining the limits of structural contraction. The \( p,n \) region in which \( \Delta f \) exceeds the free energy required for structural contraction (\( \Delta F_{op-cp} \), ca. 900 kJ mol\(^{-1}\)) matches well with the experimentally observed presence of structural contraction upon adsorption of methane (91-130 K). Please note we make a constant approximation for the free energy of structure contraction, \( \Delta F_{op-cp} \), as entropy was previously reported to have a negligible contribution to the guest-free framework transition. This obtained thermodynamic analysis of the evolution of \( \Delta n_{NGA} \) in particular the increase with decreasing temperature, is in contrast to the experimental observations. In fact, from an equilibrium thermodynamic standpoint it is impossible to predict the temperature dependence. One could argue, that \( \Delta n_{NGA} \) is expected to decrease with decreasing temperature because \( |\Delta f| \), the thermodynamic driving force for the transition, increases with decreasing temperature. In this case \( \Delta n_{NGA} \) could exhibit negative values, which would indicate a sudden jump towards higher adsorbed amount in the isotherm (Fig. ). However, this analysis is complicated by two important aspects intrinsically connected to NGA, the metastability of the transition and the desorption of gas upon structural contraction. Both features are not captured by the above methodology and thus don’t allow to draw any conclusion in the evolution of \( \Delta n_{NGA} \) with temperature. The conducted thermodynamic characterisation, however, does capture and rationalize the upper temperature limit, \( T_{high} \), for structural contraction very accurately and supports the empirical
correlation of $T_c$ and $T_{\text{NGA}}$. In the next section, we rationalise the non-monotonic NGA behaviour and estimate $\Delta n_{\text{NGA}}$ based on a different theoretical model, a mechanical model based on adsorption-induced stress.

**Adsorption-stress model for determination of low temperature limit ($T_{\text{low}}$)**

Analyzing the adsorption mechanism via *in situ* neutron diffraction and GCMC simulations, we concluded that the adsorption-induced stress occurring from adsorption in the larger pores in the DUT-49 framework precedes the structural contraction. In fact, several studies on ordered mesoporous silicates show that the adsorption-induced stress on the host material reaches a maximum value before capillary condensation occurs in the mesopores$^{2,34}$. This phase transition in the fluid phase is characterized by a hysteresis, depending on diameter of the pore. The activation barrier with decreasing adsorption temperature for capillary condensation is reported to increase and a widening of the hysteresis is observed$^{31,35,36}$. Recent computational analysis of the adsorption kinetics in carbonaceous materials demonstrated this hysteretic phenomenon$^{37}$. However, such molecular simulations in a complex pore system, such as DUT-49, are computationally very challenging. Instead, we recently demonstrated that thermodynamic and kinetic conditions for NGA can be modeled in a simple slit-pore toy model$^{15}$. Instead of directly simulating the full energy landscape of the material, here we consider NGA as a result of structural contraction induced by adsorption-induced stress. Characterizations of mechanical properties of the DUT-49 framework have estimated the critical stress for structural contraction in the range of 35 MPa, supported by experimental hydrostatic compression of DUT-49 crystals and molecular simulations$^{25}$. Rather than analyzing the metastability of NGA we decided to probe the region in which the adsorption-induced stress reaches a critical level for structural contraction. Adsorption stress isotherms were established for methane adsorption in DUT-49 using a series of classical molecular dynamics simulations in the $NVT$ ensemble. We employed these simulations for methane adsorption at three temperatures at which NGA was experimentally observed namely 91, 111 and 130 K (Fig. 6).
Fig. 6. Grand canonical Monte Carlo simulation of methane adsorption for the op and cp phases of DUT-49 at 91 K, 111 K and 130 K. (a). Adsorption-induced stress from methane adsorption in the op phase of DUT-49 computed from 10 unique NVT simulations where the mean is plotted, where standard deviations were smaller than the symbol size.

This adsorption-induced stress follows non-monotonic behavior characteristic of many mesoporous materials\(^2,38\). Although structural contraction and the presence of a metastable state beyond the crossing point of the isotherm \((n_{op} = n_{cp})\) are required for NGA, and strongly influenced by the mechanical properties of the framework, prior to this the mechanical role of the adsorbate has not been investigated. We observe that the process of methane adsorption can produce considerable adsorption-induced stress. Notably the minimum between -30 and -40 MPa compares well to the experimental transition pressures, previously reported by hydrostatic compression\(^25\). Since the structural contraction is found to be independent of temperature effects, especially in such a small temperature range, the critical stress for contraction might be assumed the same for all investigated temperatures. Similar to our previous analysis of the free energy change as a function of \(n_{op}-n_{cp}\) the adsorption stress isotherms can also be transferred as a function of \(n_{op}-n_{cp}\) (Fig. 7).
Fig. 7. a) A representation of stress-based model for adsorption-induced structural transformations in DUT-49 reprinted from reference 23. Adsorption-induced stress in the range of the crossing point of the $op$ and $cp$ isotherms computed from 100 unique NVT simulations where the mean is plotted with standard deviations depicted by opacity.

Although the slope of the stress isotherms as a function of $n_{op}$-$n_{cp}$ are comparable, they exhibit an offset towards increased $\Delta n_{NGA}$ values with increasing temperatures. To reproduce the $\Delta n_{NGA}$ observed experimentally, $\Delta n_{NGA}$ at 91K is estimated at 50 CH$_4$ per unit cell (calculated 2.6 mmol g$^{-1}$, experimental 1.36 mmol g$^{-1}$), 150 CH$_4$ per unit cell (calculated 7.9 mmol g$^{-1}$, experimental 6.1 mmol g$^{-1}$) at 111 K and 200 CH$_4$ per unit cell (calculated 10.5 mmol g$^{-1}$, experimental 0.2 mmol g$^{-1}$, estimated for complete $op$-$cp$ transition 8.3 mmol g$^{-1}$) at 130 K, the corresponding critical stress is in the range of -25 MPa to -20 MPa. This critical stress is in the same numerical range of the transition pressure (35 MPa) measured by mercury intrusion thus supporting the validity of this adsorption-stress model, which was initially tested on a very different material, namely the breathing MIL-53. Changes in adsorption temperature will influence the adsorption in both phases and as a result the crossing point is shifted towards decreasing relative pressure with a decrease in temperature. Consequently, at lower temperature the critical adsorption stress occurs at a pressure where structural contraction is thermodynamically possible but at a pressure closer to the crossing point of the $op$-$cp$ isotherms, which in consequence leads to inferior $\Delta n_{NGA}$. With increasing temperature, the transition region is shifted to higher pressure as well as higher $n_{op}$ beyond the intersection of the isotherms and thus results in enhancement of $\Delta n_{NGA}$.

**Conclusion**
In conclusion, we have demonstrated the presence of negative gas adsorption transitions upon adsorption of a series of hydrocarbons and noble gases in DUT-49 in defined temperature and pressure ranges. For each adsorptive NGA was observed in a limited temperature range $T_{\text{high}} - T_{\text{low}}$, which linearly correlates with the critical temperature of the adsorptive. An empirical correlation was determined to be universal for hydrocarbons, and noble gases, and predicts the temperature range where NGA is expected to occur in DUT-49 for fluids not investigated in this study. A non-monotonic evolution of $\Delta n_{\text{NGA}}$ with temperature was observed from the experimental isotherms, with a high temperature and low temperature limit. The thermodynamic interactions responsible for these limits were further characterised by computational methods using methane adsorption as an example. First, the high temperature limit of adsorption-induced structural contraction was analysed using the osmotic ensemble on a series of GMCM modelled isotherms. It was found that beyond a certain temperature limit the change in adsorption energetics between the $\text{op}$ and $\text{cp}$ state no longer allows for the compensation of the energy required for structural contraction. Although the computationally predicted upper temperature limit correlates well with experimental observations and thus provides a novel tool to predict structural contraction in the DUT-49 system ab initio, it provides no information on the experimentally observed lower temperature window and the evolution of $\Delta n_{\text{NGA}}$ with temperature. Because kinetic analysis of adsorption in a large system like DUT-49 is so far not accessible we instead decided to characterise the temperature dependence of the adsorption-induced stress, responsible for structural contraction. The stress minimum is found to be shifted with decreasing temperature to lower adsorption relative pressure, closer to the intersection of the isotherms of DUT-49$\text{op}$ and $\text{cp}$. Consequently, $\Delta n_{\text{NGA}}$ is found to decrease with decreasing temperature. The predicted transition pressures from the stress-based analysis correlate well with the experimental observations and allow to replicate the evolution and to some extent the magnitude of $\Delta n_{\text{NGA}}$, consequently providing an explanation for the observed non-monotonic NGA behaviour.

This present study, on the role of temperature on NGA transitions, addresses important questions. It mainly demonstrates that NGA is a physical phenomenon dictated by the combination of solid-fluid and fluid-fluid interactions and is observed for a wide array of different gases in different temperature regimes. However, this study raises two questions: First, is the empirically derived correlation between $T_{\text{NGA}}$ and $T_c$ valid for other adsorbatives that exhibit enhanced solid-fluid and fluid-fluid interactions such as CO$_2$ or other very polar gases? Secondly, is the analysis valid for other materials known to exhibit NGA, such as DUT-50, with a different pore size distributions and
can a more general correlation link these material parameters to the physical gas properties identified in the present study? Ideally, such correlations can be identified purely *ab initio* by the use of computational analysis. However so far, we were not able to compute the full energy landscape of gas adsorption in DUT-49 at different temperatures involving both entropic and enthalpic factors, occurring by the release of gas upon NGA, and the evolution of kinetic barriers, known to be responsible for NGA. These computations might also help to identify novel NGA-capable porous solids. For now, rather simplistic thermodynamic, stress-based, and empirical correlations derived from experimental analysis provide a conceptual guideline for the temperature range in which NGA is to be expected, possibly in systems other than DUT-49. For example, generally lower adsorption temperatures benefit structural contraction, by enhanced adsorption-induced stress, and thus present one of the prerequisites for NGA to occur.

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39. **Conflicts of interest**

   There are no conflicts to declare.

40. **Acknowledgements**

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**Electronic supplementary information**

Additional experimental details, synthesis procedures as well as adsorption isotherms and in situ PXRD data can be obtained from the supplementary information.
Supplementary information for
The Role of Temperature and Adsorbate on Negative Gas Adsorption in the
Mesoporous Metal-Organic Framework DUT-49

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1. Materials and methods

The synthesis and characterization of this DUT-49 sample used in the presented experiments is in detail described in reference \(^1\) where it is labelled as DUT-49(4). All samples used in the conducted study originate from the same batch of DUT-49 crystals with an average crystal size distribution of 4.26 µm. The following gases were used:

**Supplementary Table 1. List of gases used for adsorption experiments.**

| Name      | purity   | Manufacturer |
|-----------|----------|--------------|
| Helium    | 99.99%   | Linde        |
| Argon     | 99.995%  | Linde        |
| Krypton   | 99%      | Linde        |
| Xenon     | 99.95%   | Linde        |
| Methane   | 99.995%  | Linde        |
| Ethene    | 99.9%    | Linde        |
| Ethane    | 99.9%    | Linde        |
| \(n\)-Propane | 99.95% | Linde        |
| \(n\)-Butane | 99.95 | Linde        |
| \(iso\)-Butane | 99.95 | Praxair      |
| 1,3-Butadiene | 99%    | Linde        |
| Hydrogen  | 99.95%   | Linde        |

*Supplementary Table 2. List of solvents used for vapour adsorption experiments.*

| Name      | purity        | Manufacturer   |
|-----------|---------------|----------------|
| \(n\)-Pentane | 99% anhydr.   | Sigma Aldrich  |
| \(n\)-Hexane  | 99% anhydr.   | Sigma Aldrich  |
| \(n\)-Heptane | 99% anhydr.   | Sigma Aldrich  |
2. Low pressure adsorption experiments (<110 kPa)

Low pressure ($p < 110$ kPa) volumetric adsorption experiments were carried out on a BELSORP-max instrument by MICROTRACBEL CORP. and the measuring routine of BELSORP-max control software was used. In general, equilibration conditions for each point were 1% pressure change within at least 350 s. For adsorption experiments below the standard boiling point of the adsorptive 1% within 500 s was chosen. The dead volume was routinely determined using helium. Values for the adsorbed amount of gas in the framework are all given at STP and were recalculated to mmol g$^{-1}$.

Prior to the measurement the samples were degassed at 373-423 K for at least 5 h in dynamic vacuum ($p < 10^{-4}$ kPa).

Vapor adsorption experiments were conducted at 298 K using the BELSORP-max routine for degassing and characterization of vapors. Equilibration criteria were increased to 0.5% pressure change within at least 550 s due to the low pressures and relatively slow equilibration in these experiments.

Several methods for reaching the desired adsorption temperatures were used: For analysis at 295 K or higher temperatures a JULABO thermostat was used. For analysis at 273 K ice was used as a coolant. To reach adsorption temperatures not achievable by these techniques in the range of 300 K – 10 K a closed cycle helium cryostat was used. The cryostat DE-202AG was operated by a temperature controller LS-336 (LAKE SHORE) and the heat produced by the cryostat is removed from the system by a water-cooled helium compressor ARS-2HW. The sample was placed in a custom made cell consisting of a 3 cm long rod-shaped copper cell of 1 cm diameter, sealed by a copper gasket from the exterior with a copper dome and insulated by dynamic vacuum ($p < 10^{-7}$ kPa), and connected to the BELSORP-max adsorption instrument with a 0.5 mm copper capillary. The samples were degassed prior to the measurement at room temperature for at least 1 h in dynamic vacuum ($p < 10^{-7}$ kPa).
3. High pressure adsorption experiments (1 kPa< $p$ < 8 MPa)

High pressure (1 kPa< $p$ < 8 MPa) volumetric adsorption experiments were carried out on a BELSORP-HP instrument by MICROTRACBEL CORP. and the measuring routine of BELSORP-HP control software was used. In general equilibration conditions for each point were 1% pressure change within at least 350 s (exceptions are mentioned specifically). The dead volume was routinely determined using helium at 298 K and at the desired adsorption temperature. The adsorption temperatures in the range of 300 K – 10 K were achieved by using the same closed cycle helium cryostat described in detail above. The sample was placed in a custom-made cell consisting of 3 cm long copper-mantled VCR-sealed stainless-steel SWAGELOK cell of 0.5 cm inner diameter and connected to the BELSORP-HP adsorption instrument with a 0.5 mm stainless steel capillary. The cell was insulated by dynamic vacuum ($p < 10^{-4}$ kPa), and the samples were degassed prior to the measurement at room temperature for at least 1 h in dynamic vacuum ($p < 10^{-5}$ kPa). Adsorbed amounts are given as excess amount adsorbed in mmol g$^{-1}$. 
4. Routine for sample recycling

In our previous studies on NGA the transition upon desorption was found to be irreversible. Consequently, for each adsorption measurement a new sample of DUT-49 had to be used to record individual isotherms. To overcome this extensive usage of sample amount a routine was developed to cycle DUT-49 even when NGA is present. This procedure was previously described in two references and was primarily applied in the characterization of methane and ethane for which experiments were first conducted at elevated temperatures and then stepwise decreased until structural transitions were observed and then after desorption the regeneration protocol applied.

In general, some adsorbed molecules can be removed from the pores of DUT-49 if the guest molecules are in a supercritical state. This fact is used in the initial supercritical activation of DUT-49 using carbon dioxide. When analyzing the adsorption behavior upon adsorption of methane it becomes obvious that the isotherms become reversible at temperatures beyond the critical point (for methane around 150 K). Thus, methane can be removed from the pores of DUT-49 by increasing the temperature beyond this point while maintaining saturation pressure in the measuring cell. This method of regeneration has some experimental limitations: The increase in temperature while maintaining saturation pressure of the adsorptives can lead to high pressures. Thus, this method of regeneration could only be performed in high pressure equipment. For experiments conducted at pressures below 100 kPa in the BELSORP-max instrument, each experiment was performed on a fresh sample. In addition, this recycling technique was found to be not applicable to adsorption of krypton, propane, n-butane (due to limitations of upper temperature limit of the instrument) and ethene.
5. Adsorption isotherms

In the following figures adsorption isotherms of different gases/vapors and recorded at different temperatures are depicted. In each isotherm filled symbols correspond to the adsorption, empty symbols to the desorption carried out subsequently.
Supplementary Figure 1. Adsorption (closed circles) and desorption (open circles) isotherms of a) n-heptane, b) n-hexane, c) n-pentane, d) n-butane, e) n-propane, f) ethane, g) ethene, h) methane, and i) hydrogen at their respective boiling points with the exception of vaporized n-pentane-n-heptane in DUT-49) j) Molar density of fluid adsorptive at adsorption temperature and saturation pressure, methane and ethene are the only two gases to show NGA.
Supplementary Figure 2. Adsorption isotherms of methane in DUT-49 at a) 91-130 K and b) 140-190 K including 111 K for comparison.
Supplementary Figure 3. Methane adsorption/desorption isotherms on DUT-49 at a) 91 K, c) 101 K, e) 111 K, g) 120 K, b) 125 K, d) 130 K, f) 135 K, and h) 150 K. Adsorption in closed symbols, desorption in open symbols.
Supplementary Figure 4. Adsorption (closed symbols) and desorption (open symbols) isotherms of ethene at a) 169 K, b) 179 K, c) 189 K, and d) 199 K in DUT-49.

Supplementary Figure 5. Adsorption (closed symbols) and desorption (open symbols) isotherms of ethane at a) 184 K, b) 190 K, c) 200 K, d) 210 K, e) 220 K, f) 230 K, g) 240 K, h) 250 K, and i) 270 K in DUT-49.
Supplementary Figure 6. Adsorption (closed symbols) and desorption (open symbols) isotherms of propane at a) 231 K, b) 240 K, c) 250 K, d) 261 K, e) 270 K, and f) 298 K in DUT-49.

Supplementary Figure 7. Adsorption (closed symbols) and desorption (open symbols) isotherms of n-butane at a) 273 K, b) 288 K, c) 298 K, and d) 308 K in DUT-49.
Supplementary Figure 8. Adsorption (closed symbols) and desorption (open symbols) isotherms of 1,3-butadiene at a) 273 K, b) 298 K, and c) 303 K in DUT-49.

Supplementary Figure 9. Adsorption (closed symbols) and desorption (open symbols) isotherms of a) n-butane (yellow), b) 1,3-butadien (green), c) iso-butane (blue), and comparison of adsorption branches at 298 K.

Supplementary Figure 10. Adsorption (closed symbols) and desorption (open symbols) isotherms of a) argon at 87 K, b) krypton at 120 K, c) xenon at 165 K, and d) direct comparison of the adsorption branches.
Supplementary Figure 11. Adsorption (closed symbols) and desorption (open symbols) isotherms of argon at a) 77 K, b) 87 K, c) 97 K, and d) 100 K, e) 105 K, and f) 110 K.
Supplementary Figure 12. Adsorption (filled symbols) and desorption (empty symbols) isotherms of krypton at a) 120, b) 130 K, c) 140 K, d) 150 K, and e) 160 K.

Supplementary Figure 13. Adsorption (filled symbols) and desorption (empty symbols) isotherms of xenon at a) 165, 175, and 190 K, b) 195 and 200 K, c) 210, 215, 237 K, and d) 230 and 237 K.
6. Empirical analysis of NGA parameter

NGA parameter were derived from the previously shown isotherms. In the table below numerical values relevant for the discussion of the manuscript are provided in Supplementary Table 3. It is important to note that adsorption experiments may suffer from errors primarily caused by variations in the sample amount and inaccurate weighing caused by the preparation under inert atmosphere. A second inaccuracy originated from the resolution of the isotherms which, in the case of high pressure isotherms, strongly relies on the sample amount used in the experiment. This inaccuracy is expected to result in an underestimation of $\Delta n_{\text{NGA}}$. Temperature accuracy in the conducted experiments was determined by internal calibration via condensation of the fluid at saturation pressure. The instrument itself provides a high temperature stability and accuracy of 0.01 K.

Supplementary Table 3. Numerical values to describe NGA properties derived from the recorded isotherms. contains the adsorption temperature, $T$, the adsorbed amount in the $op$ phase before NGA, $n_{op}(\text{NGA})$, the adsorbed amount in the $cp$ phase after NGA, $n_{cp}(\text{NGA})$, the amount of gas expelled upon NGA expressed as $\Delta n_{\text{NGA}}$, as well as the pressure at which NGA occurs, $p_{\text{NGA}}$, recorded at $n_{op}(\text{NGA})$. 
Supplementary Table 3. Numerical values to describe NGA properties derived from the recorded isotherms.

| Gas          | $T$  | $n_{op}$ (NGA) (mmol g$^{-1}$) | $n_{cp}$ (NGA) (mmol g$^{-1}$) | $\Delta n_{NGA}$ (mmol g$^{-1}$) | $p_{NGA}$ (kPa) |
|--------------|------|--------------------------------|-------------------------------|----------------------------------|----------------|
| Methane      | 91   | 27.82                          | 26.45                         | 1.37                             | 1.23           |
|              | 101  | 30.96                          | 24.67                         | 6.28                             | 4.23           |
|              | 111  | 28.15                          | 22.93                         | 6.12                             | 9.39           |
|              | 120  | 30.09                          | 24.70                         | 5.39                             | 21.62          |
|              | 125  | 29.36                          | 24.71                         | 4.66                             | 31.53          |
|              | 130  | 33.061                         | 32.99                         | 0.07                             | 52.87          |
| Ethene       | 169  | 17.60                          | 16.37                         | 1.23                             | 10.25          |
|              | 179  | 17.69                          | 15.64                         | 2.05                             | 20.29          |
|              | 189  | 20.57                          | 14.54                         | 6.02                             | 40.67          |
|              | 199  | 22.41                          | 14.33                         | 8.08                             | 71.01          |
| Ethane       | 200  | 15.14                          | 14.92                         | 0.22                             | 29.44          |
|              | 210  | 17.27                          | 14.85                         | 2.42                             | 52.03          |
|              | 220  | 18.86                          | 14.83                         | 4.02                             | 84.75          |
|              | 230  | 20.42                          | 18.93                         | 1.49                             | 132.9          |
|              | 240  | 23.35                          | 23.27                         | 0.08                             | 216.3          |
| Propane      | 261  | 12.12                          | 10.35                         | 1.76                             | 45.61          |
| $n$-Butane   | 288  | 9.21                           | 8.86                          | 0.35                             | 22.38          |
|              | 298  | 9.90                           | 8.59                          | 1.31                             | 31.51          |
|              | 308  | 12.55                          | 9.43                          | 3.12                             | 46.24          |
| 1,3-Butadiene| 298  | 10.64                          | 9.07                          | 1.57                             | 37.05          |
|              | 303  | 12.85                          | 9.71                          | 3.13                             | 46.56          |
| 2-Methylpropane| 298 | 46.24                          | 9.75                          | 3.76                             | 46.73          |
| Argon        | 77   | 33.35                          | 32.19                         | 1.15                             | 3.714          |
|              | 87   | 37.69                          | 31.43                         | 6.26                             | 13.12          |
|              | 97   | 43.12                          | 31.77                         | 11.3                             | 43.68          |
|              | 100  | 45.24                          | 35.75                         | 9.49                             | 43.26          |
| Krypton      | 120  | 26.93                          | 25.04                         | 1.88                             | 16.63          |
|              | 130  | 26.73                          | 23.01                         | 3.72                             | 26.08          |
|              | 140  | 34.36                          | 28.13                         | 6.23                             | 53.84          |
|              | 150  | 28.67                          | 23.58                         | 5.09                             | 100.53         |
| Xenon        | 195  | 21.5                           | 17.64                         | 3.85                             | 76.55          |
|              | 200  | 20.13                          | 17.37                         | 2.75                             | 75.82          |
|              | 210  | 18.29                          | 17.89                         | 0.39                             | 112.21         |
|              | 215  | 16.18                          | 16.06                         | 0.12                             | 134.95         |
Critical temperatures, $T_c$, and standard boiling points, $T_b$, of the gases used in the experiments were obtained from the NIST Chemistry webBook SRD 69 (https://webbook.nist.gov/chemistry/fluid/) and are listed in the following table.

Supplementary Table 4. Critical temperatures and standard boiling points of gases used in the experiments.

| Gas            | Critical temperature, $T_c$ (K) | Standard boiling point, $T_b$ (K) |
|----------------|---------------------------------|----------------------------------|
| Methane        | 190.6                           | 111.7                            |
| Ethene         | 282.3                           | 169.4                            |
| Ethane         | 305.3                           | 184.5                            |
| Propane        | 369.8                           | 231                              |
| $n$-Butane     | 425.1                           | 272.6                            |
| 1,3-Butadiene  | 425.1                           | 268.8                            |
| 2-Methylpropane| 407.8                           | 261.4                            |
| Argon          | 150.7                           | 87.3                             |
| Krypton        | 209.5                           | 119.7                            |
| Xenon          | 289.7                           | 165                              |

Supplementary Figure 14. Temperature-depending presence and magnitude of $\Delta n_{NGA}$ in DUT-49 for different hydrocarbons. a) Linear saturated hydrocarbons with respective boiling points indicated as dashed vertical lines, b) butane derivatives at near ambient temperatures.
Supplementary Figure 15. $T_{NGA}$ plotted over a) critical temperature, b) standard boiling point, and c) reduced temperature. Linear fits for each plot and error bars are provided.

Supplementary Figure 16. Relationship of critical pressure $p_c$ and relative pressure of NGA $p_{NGA}/p_0$, for all presented gases including parameters for linear fit.
7. **In situ PXRD Experiments**

PXRD experiments in parallel to adsorption were performed at BESSY II light source, KMC-2 beamline of Helmholtz-Zentrum Berlin für Materialien und Energie using the recently established experimental setup. The diffraction experiments were performed in transmission geometry using a sample holder with a thickness of 2 mm. Monochromatic radiation with energy of 8048 eV ($\lambda = 1.5406$ Å) was used for all experiments. The diffraction images were measured using 2$\theta$ scan mode and a Vantec 2000 area detector system (BRUKER) in the range of 2 – 50° 2$\theta$. A synchrotron beam with dimensions of 0.5 x 0.5 mm was used for the experiments. Corundum powder with a crystallite size of 5 µm was used as an external standard. The image frames were integrated using Datasqueeze 2.2.9 software and processed using Fityk 0.9.8 program.

To control the gas loading the BELSORP-max setup was used. The adsorption chamber was sealed with an X-ray transparent beryllium dome and connected to the BELSORP-max via a 0.5 mm copper capillary. The adsorption cell was isolated by a second beryllium dome and insulating dynamic vacuum ($p < 10^{-5}$ kPa). Different gas loadings were dosed to the cell and equilibrated by using either the automated BELSORP software while automatically recording a full isotherm or by manually dosing. The gas pressure was equilibrated for at least 400 s before a PXRD pattern was recorded in both cases. The adsorption temperature was controlled by a closed cycle helium cryostat. The cryostat DE-202AG was operated by a temperature controller LS-336 (LAKE SHORE) and the heat produced by the cryostat is removed from the system by a water-cooled helium compressor ARS-2HW.

Temperature dependent PXRD experiments were performed in a closed chamber under dynamic vacuum of $10^{-4}$ mbar in the temperature range of 100 – 725 K with steps of 25 K on a PANALYTICAL X'PERT PRO with $\lambda = 0.15405$ nm in Bragg-Brentano-geometry. The temperature was raised with 5 K min$^{-1}$ starting at 100 K. For each temperature three PXRD patterns were collected under isothermal conditions in the 2$\theta$ range from 2.5 up to 22 °, with a step size of 0.028 ° and 40 s per step.
Supplementary Figure 17. *In situ* PXRD in parallel to propane physisorption at 231 K of DUT-49: Adsorption-desorption isotherm (a), selected points are labeled by numbers. Filled symbols correspond to adsorption, empty symbols to desorption. b) PXRD patterns, color code: DUT-49cp (orange) DUT-49ip (green), and DUT-49op (blue).
Supplementary Figure 18. In situ PXRD in parallel to ethane physisorption at 185 K of DUT-49: Adsorption-desorption isotherm (a), selected points are labeled by numbers. Filled symbols correspond to adsorption, empty symbols to desorption. b) PXRD patterns, color code: DUT-49cp (orange) DUT-49ip (green), and DUT-49op (blue).
Supplementary Figure 19. PXRD patterns simulated for DUT-49cp (blue), an in situ pattern of methane adsorbed at DUT-49 at 111 K and 14 kPa (green), ethane adsorbed at 185 K and 21.6 kPa (orange), propane adsorbed at 231 K and 13 kPa (red), and n-butane adsorbed at 298 K and 41 kPa (dark blue). b) Enlargement of low angle region.
8. Simulation methods

Grand canonical Monte Carlo (GCMC) simulations used the RASPA2.0 code and simulated the adsorption for previously reported op and cp structures of DUT-49. Each isotherm was simulated with an equilibration of $5 \times 10^5$ cycles and the subsequent $1 \times 10^6$ cycles were sampled, for each pressure point. A total of 50 pressures were investigated for each temperature and were uniformly distributed in log space between $1 \times 10^{-2}$ Pa and $5 \times 10^6$ Pa. For each simulation, the van der Waals interactions for the framework used the UFF force field and methane the united-atom TraPPE force field. Parameters for framework-gas interactions were obtained by Lorentz–Berthelot mixing rules. No charges were considered for the framework atoms.

We computed the osmotic ensemble from interpolation of the simulated isotherms. In particular, we consider the difference in osmotic potential between the op and cp forms ($f_i$), without considering the difference in energy of the host. This provides the energy gained by the phase transformation op $\rightarrow$ cp.

Adsorption stress was simulated using the MOF-FF and united-atom TraPPE force fields to describe DUT-49 and methane, respectively. Trajectories were computed in the NVT ensemble, using lammps, employing the Nose-Hoover thermostat with a dampening parameter of 100 fs and a timestep of 1 fs. Starting configurations were obtained from snapshots of GCMC simulations, described previously, and 10 unique configurations were sampled for each loading. The trajectories were simulated for a total of 1000 ps and the last 500 ps were used for sampling the total stress of the system. To provide greater precision in the area of NGA, 16 loadings between 400 and 700 methane molecules were simulated, using the same methodology, however, 50 unique configurations were sampled.

Please note, raw data and representative input files for molecular simulations described here are available online in our data repository at https://github.com/jackevansadl/supp-data.
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