Kinetics and enthalpies of methane adsorption in microporous materials AX-21, MIL-101 (Cr) and TE7

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**Highlights**

* Kinetics of methane adsorption in activated carbons AX-21 and TE7 and MOF MIL-101 are analysed.
* Mass transfer coefficients, effective diffusivities and activation energies are calculated.
* Enthalpies are estimated with Clausius-Clapeyron equation for absolute and excess adsorption.
* These are compared with differential calorimetry, with differences up to 3.5 kJ mol-1.

**Abstract**

Methane is touted as a replacement for fossil fuels in transport applications due to its lower costs of production and cleaner combustion. Storage of methane is still a problem and different technologies have been considered, including compression and liquefaction. Adsorption in a porous material is a potential alternative for methane storage, as it can increase densities at moderate pressures and temperatures. For practical applications, in addition to the quantities stored and working capacities, it is important to equally consider aspects such as kinetics of storage and thermal management of the storage system. In this paper, the kinetics and enthalpies of adsorption of methane in activated carbons AX-21 and TE7, and metal-organic framework MIL-101 (Cr) are extracted from readily available gas sorption data. The adsorption kinetics at 300 K and 325 K are analysed and fitted with the linear driving force (LDF) model, and mass transfer coefficients (MTC) and effective diffusivities are estimated. The effective diffusivities have a range of values from 1.79 x 10-13 m2 s-1 for the MIL-101 (Cr) at 300 K to 9.36 x 10-10 m2 s-1 for the TE7 at 325 K. The activation energies for the effective diffusivities based on an Arrhenius-type temperature dependence are calculated as 7.42, 7.09 and 5.38 kJ mol-1 for the AX-21, the MIL-101 (Cr) and the TE7, respectively. The enthalpies of adsorption are calculated with the Clausius-Clapeyron equation and the differences observed when calculating these with excess and absolute amounts are presented and discussed, with the results showing that enthalpies can have up to 10% differences if using excess amounts instead of absolute quantities. The isosteric enthalpies are also compared with enthalpies at zero-coverage obtained from differential calorimetry experiments for the MIL-101 (Cr), and a ~3.5 kJ mol-1 difference is observed, which underlines the importance of refining calculation methods and bridging the gap between direct and indirect methods for calculating enthalpies of adsorption.

**Keywords**: methane storage; methane adsorption; kinetics; enthalpies of adsorption.

**Introduction**

Natural gas, i. e., a hydrocarbon-rich gas that can be found on oil fields, natural gas fields and coal beds, is one of the fastest growing sources of primary energy in the world [[1](#_ENREF_1)]. Natural gas is considered a cleaner alternative to diesel or petrol (gasoline) for internal combustion engines in transport applications, as it emits 30 % less carbon dioxide per unit energy, due to the fact that methane (the main constituent of natural gas, usually with >90% concentration) is the hydrocarbon with the highest hydrogen-to-carbon ratio [[2](#_ENREF_2)]. However, it should be noted that natural gas is not a long-term solution for environmental issues and anthropogenic climate change. Methane, the main constituent of natural gas, is a more potent greenhouse gas than carbon dioxide, and increased use of methane will mean that there will likely be more leakages to the atmosphere [[3](#_ENREF_3)].

Despite presenting some advantages, using natural gas in transport applications still suffers from technical problems, especially related to the storage of the gas on-board the vehicle. On a mass basis, methane has a combustion enthalpy (55.5 MJ kg-1) that is slightly higher than that of gasoline (46.4 MJ kg-1) or diesel (45.6 MJ kg-1), but unlike liquid petrol or diesel, natural gas is a low-density gas at ambient temperatures and pressures, resulting in low energy density per unit volume in these conditions. To guide research in this area, the US Department of Energy (DOE) has set targets for onboard storage of methane, which are set at a methane density of 350 v/v (STP) at room temperature and 6.5 MPa, recently updated from the previous target of 263 v/v (STP) [[4](#_ENREF_4), [5](#_ENREF_5)].

To increase its density, methane is usually compressed to 25 MPa, requiring thick and heavy cylinders which are difficult to fit inside light-duty vehicles. Compressing to these pressures also carries an associated cost [[6](#_ENREF_6)]. Other alternatives have been considered, including liquefaction of natural gas, but this requires cooling down and maintaining temperatures below 111 K. The need for lower temperatures also entails a cost, requires well-insulated expensive tanks, and presents significant safety issues [[6](#_ENREF_6)] due to pressurisation due to natural gas boil-off if vehicles are left dormant for long periods.

This has prompted research into different alternatives for increasing the density of natural gas. One alternative is to adsorb natural gas into porous materials, increasing the volumetric density of the gas at moderate pressures and temperatures. Adsorbed natural gas (ANG) has some advantages over conventional methods, as it allows for more natural gas to be stored at lower pressures, which allows for lighter, more conformable tanks to be used [[7](#_ENREF_7)]. This has driven much research on porous materials for storage of natural gas and its main constituent methane, with different materials proposed as ideal methane or natural gas stores.

**Porous materials for methane storage**

A number of porous materials have been proposed to store methane, with some of the most promising studies being on adsorption into activated carbons or metal-organic frameworks [[6](#_ENREF_6)]. Metal-organic frameworks (MOFs) are materials made from coordinated metal clusters with organic linkers, which can be synthesised with tuneable porosities and high surface areas. MOFs that have been investigated for methane storage include HKUST-1 and Ni-MOF-74, which have shown some of the highest total volumetric uptakes at 6.5 MPa and room temperature to date, at 267 and 251 v/v (STP), respectively [[8](#_ENREF_8)]. The recently revised DOE targets for methane storage in adsorbent materials consist of 0.5 g CH4 per g of sorbent (gravimetric capacity) and a 263 cm3 of CH4 per cm3 of adsorbent (volumetric), so the materials would meet or be very close to meeting volumetric targets. These materials also displayed good volumetric working capacities of 190 and 129 v/v (STP) for HKUST-1 and Ni-MOF-74, respectively [[8](#_ENREF_8)]. Large-scale computational studies have also been used to guide materials synthesis. A study by Wilmer *et al.* of hypothetical and synthesised MOFs has highlighted the potential of these materials for methane storage and identified 300 materials that have methane storage capacities higher than 230 v/v (STP). It also highlighted that the metric that more closely correlates with methane volumetric storage is the volumetric surface area [[9](#_ENREF_9)]. Recently, a sol-gel process was reported for making monolithic HKUST-1, which showed excellent methane capacities, with a volumetric uptake of 259 v/v (STP) [[10](#_ENREF_10)]. Our own work showed that high surface area materials such as AX-21, TE7 and MIL-101 (Cr) can have adsorbed densities that are equal to the liquid density of methane and can rival the densities of methanol, with working capacities close to 140 v/v (STP) for charging at 6.5 MPa and discharging at 0.5 MPa and 250 K [[11](#_ENREF_11)].

In addition to capacities, there other significant challenges of using porous materials for methane storage, which include stability of the adsorbent material, thermal management of the adsorbent system, composition of natural gas/purity of methane, adsorption and desorption kinetics, and scale-up/cost of materials [[12](#_ENREF_12)]. The kinetics of adsorption are particularly relevant for the charging and discharging times, as they will influence the refuelling times. Oil and diesel can be fuelled quickly in vehicles (around 40 L per minute, equivalent to 20 MW of power), whereas compressed natural gas systems refill around 55 L in 5 minutes [[2](#_ENREF_2)]. If ANG systems are to be used in mobile applications, it is important to have systems that can quickly refill, and the DOE has set a specific delivery rate higher than 2.6 kW L-1 for the whole storage system for onboard storage of methane [[4](#_ENREF_4)]. Thus, although it is important to look at the kinetics of methane adsorption in the different materials, they are challenging to extract; thus, these figures are rarely reported [[13](#_ENREF_13)]. Thermal management is another key consideration, due to the large amounts of heat released when adsorbing gases on porous materials resulting from the very temperature-dependent exothermic adsorption process. Thermal management is critical for ANG systems, as temperature changes of around 373 K have been seen in activated carbon ANG systems [[6](#_ENREF_6), [14](#_ENREF_14), [15](#_ENREF_15)], which is then reflected in much reduced methane capacities.

In this work, we investigate two important aspects of adsorptive methane storage: kinetics, which are relevant for the fast charge and discharge of methane in porous materials, and enthalpies, which are important for the thermal management of the system, for a range of model materials [AX-21, MIL-101 (Cr) and TE7], to compare approaches for calculation and measurement of these important parameters. We used readily-accessible gas sorption data from a volumetric gas sorption instrument to determine the mass transfer coefficients and the effective diffusivities for methane, calculated with the Linear Driving Force (LDF) model applied to experimental kinetic data for temperatures close to room temperature (300 and 325 K). We also investigate the isosteric enthalpies of adsorption obtained from experimental methane sorption isotherms for a wide range of temperatures (250 – 350 K), comparing both the enthalpies calculated with the excess and the absolute isotherm, highlighting the differences in the results from these two approaches. Finally, we compare the enthalpies of adsorption determined from the isosteric method with the zero-coverage enthalpy for the MIL-101 (Cr) obtained from direct measurement via differential scanning calorimetry.

**Experimental methodology**

The chosen model materials were AX-21, MIL-101 (Cr) and MAST TE7 carbon beads, which were selected as example materials due to their high surface areas, different pore structures, surface chemistries and cost. Details of the materials are included in the Supporting Information. We have obtained pore size distributions for all three materials using the nitrogen adsorption isotherm at 77 K and DFT methods assuming a slit pore geometry, which we reported in our previous work [[11](#_ENREF_11)]. The pore size distribution for AX-21 showed most of the pore sizes in the micropore region, with pore sizes of 0.5, 0.6, 0.8, 1.2, 1.8 and 2.2 nm. The pore size distribution for MIL-101 (Cr) was mostly around three pore sizes, with 1.3, 2.2 and 2.9 nm. As reported in the literature [[16](#_ENREF_16)], MIL-101 (Cr) has a trimodal pore size distribution, but the sizes are slightly different to the ones we are reporting, as pore sizes obtained from crystallography are 0.7, 2.9 and 3.4 nm. Finally, TE-7 has a pore size distribution with most sizes around 0.7, 0.9, 1.2 nm and some bigger pores in the macropore range (20 and 40 nm). Table 1 summarises the BET surface areas, pore volumes as determined by nitrogen adsorption at 77 K and the Dubinin-Radushkevich (DR) method, the particle sizes and the methane adsorbed densities as calculated in our previous work.

**Table 1**. Characterisation of AX-21, MIL-101 (Cr) and TE7. The BET surface areas were determined using the consistency criteria reported by Rouquerol et al. [[17](#_ENREF_17)] for nitrogen isotherms at 77 K, the micropore volumes were determined from the nitrogen isotherm at 77 K and the DR method, the skeletal volumes were determined from helium pycnometry on a degassed sample, the particle sizes were determined through SEM and Image J (assuming a spherical particle) and the adsorbed methane densities were determined in our previous work [[11](#_ENREF_11)].

|  |  |  |  |
| --- | --- | --- | --- |
| Material | AX-21 | MIL-101 (Cr) | TE7 |
| BET surface area /  m2 g-1 | 2550 ± 30 | 2520 ± 50 | 1299 ± 7 |
| Micropore volume /  cm3 g-1 | 1.97 ± 0.01 | 0.813 ± 0.003 | 0.520 ± 0.002 |
| Skeletal density /  g cm-3 | 2.67 ± 0.02 | 1.9 ± 0.3 | 2.29 ± 0.01 |
| Average particle size / µm | 3.55 | 5.57 | 210 |
| Adsorbed methane density /  kg m-3 | 503 ± 12 | 407 ± 7 | 462 ± 6 |

**Kinetic Data**

Determining transport coefficients in microporous materials can be a highly complex task, as it is difficult to achieve ideal experimental conditions and there are a multitude of rate processes that influence sorption uptake, including external mass fluxes and film resistances, heat release processes, inter and intracrystalline diffusion, thermal surface barriers and others [[18](#_ENREF_18)]. A variety of methods has been applied to study diffusion in microporous materials, including zero-length column methods, NMR pulsed-field gradient or quasi-elastic neutron scattering experiments, and computational methods such as molecular dynamics [[18](#_ENREF_18)].

In our study, kinetic parameters from adsorption equilibrium isotherms were estimated from data obtained in the Hiden HTP-1 (Hiden Isochema, Warrington, UK), a volumetric apparatus (also known as manometric, constant volume/variable pressure or piezometric method), from 250 K to 350 K and at pressures up to 15 MPa.

In a volumetric experiment, a pressure step is introduced in the sample chamber, and the pressure will change in the cell, due to adsorption of the gas by the sample as a function of time. The sample chamber is in equilibrium just before the pressure change and the mass transfer from the bulk into the sample is driven by this pressure step. In volumetric experiments, the amounts adsorbed are calculated based on this pressure difference, as the skeletal density and the volume of the chamber are known, meaning that a mass balance can be used to calculate adsorbed amounts. The Hiden HTP-1 has a cylindrical reactor for the sample, which can typically hold around 200 mg of sample material. Gas from the methane cylinder enters the instrument through a system of pressure-controlled valves, and the volume of gas to be dosed to the sample is thermally equilibrated in the system in the “settling” time. This volume of gas is then dosed to the sample reactor via a pressure-controlled valve which is positioned very close to the reactor. There is a very accurate pressure transducer close to the reactor to measure the reactor pressure, which is then used to calculate the gas uptake. Further details of the instrument and kinetic data are supplied in Supporting Information. The equilibrium data, analysis conditions, degassing of samples and other experimental aspects for all three materials have been published and analysed before in our previous work [[11](#_ENREF_11)]. For every equilibrium point, there are kinetic data available from the instrument which can be analysed, and we have used the same methodology to analyse hydrogen kinetic data in the AX-21 and MIL-101 (Cr) previously [[19](#_ENREF_19)].

In order to be able to use volumetric gas sorption to extract kinetic data, we employed some simplifying assumptions, for instance, ignoring external rate-limiting processes and assuming that the strongest resistance to mass transfer comes from narrow channels in micropores, as noted in zeolite research [[18](#_ENREF_18)]. We also assumed experimental conditions to be ideal. There can be issues with some of these approximations, namely since the highest mass fluxes will occur when there are the most deviations from ideality [[18](#_ENREF_18)]. There are also other issues when analysing kinetics in a volumetric system, for instance, valve response and opening times, volume changes within finite times, concentration changes in finite periods, etc., [[18](#_ENREF_18)] but these are difficult to completely control in a volumetric instrument. Also, to be able to accurately describe these in a kinetic model would vastly complicate it, ending up with a number of non-linear coupled partial differential equations that would require very sophisticated numerical methods [[18](#_ENREF_18)]. While there may be more accurate methods for measuring kinetics in porous materials, including NMR, zero length column methods and the others, the aim of this study was to show how kinetic information can be extracted using a simple model from measured equilibrium isotherms and where kinetic data can be easily accessed. However, it should be noted that there are limitations that need to be considered for kinetic analysis in volumetric instruments, especially when looking at strongly adsorbed and fast diffusing species such as methane [[20](#_ENREF_20)].

In order to mitigate these and approximate ideal conditions as much as possible, the following was observed for the data presented in this paper:

* Isothermal conditions – the Hiden HTP has a tight temperature control system, which maintains temperature in the reactor to within 0.1 K of the target. There is a thermocouple in the sample cell to measure sample temperatures, which are shown with the kinetic data. However, it should be noted that due to the highly exothermic nature of methane adsorption, the highest uptakes will correspond to the largest thermal variations in the sample cell.
* Thermal equilibration – the dosed gas is thermally equilibrated with the sample cell before being dosed (this usually takes a few minutes to achieve), to mitigate any thermal equilibration issues from a temperature difference between the dosed gas and the sample cell temperature. This way, the temperature changes observed in the sample cell are most likely due to heat released by the material upon adsorption.
* Opening of valves - the volumetric method has been claimed to be the best approach for transient methods (that is, when a sample is subjected to a change in pressure) when calculating intracrystalline diffusion, with the major caveat being the time constant of the valve [[18](#_ENREF_18), [20](#_ENREF_20)]. There is a very accurate pressure transducer in the dosing chamber that measures the pressure inside the sample chamber. We are aware that there are constraints for fast diffusing species and any small error in the measurements in the initial section of the kinetic curve would lead to large differences in the calculated mass transfer coefficients, and this section of the kinetic curve is strongly influenced by how the valve is opened [[20](#_ENREF_20)]. The valves in the Hiden HTP are stainless steel springless diaphragm valves for high performance (Swagelok, Solon, OH, USA) that are pneumatically actuated and, for this analysis, we are assuming that these valves are ideal, *i.e.*, they have a zero opening time. Also, as noted in the literature, in order to have a completely reliable analysis, there should ideally be two pressure transducers, one in the dosing chamber and another in the sample chamber, so that any issues related to the flow of gases through the valve can be ignored [[20](#_ENREF_20)]. For these measurements, there is only one very accurate pressure transducer in the dosing chamber (before the valve that opens to the sample) that measures the pressure inside the sample chamber.

Related to this, there are other issues associated with diffusion of very fast species such as methane, including the resolution of the pressure transducer. The equipment records the kinetic data at irregular intervals, and the recording of data is related to how the equipment calculates the sample chamber reaching equilibrium conditions. As an example, for all of the kinetic data shown in Figure 2 for the AX-21 at 300 K in the 1st pressure step (0.33 MPa), the average time interval is 14 seconds, but this is skewed by larger time intervals after 140 mins. For the first 15 kinetic points, which are the most critical for the kinetic fits, the average time interval is 0.54 seconds, with the lowest time interval being 0.3 seconds and the highest being 0.78 seconds.

**Modelling kinetic data**

Diffusion in the pores depends on pore size, sorbate concentration and other conditions. In small pores, the diffusing molecule never escapes the force field of the adsorbent surface, so transport occurs by an activated process involving jumps between adsorption sites, which is called surface diffusion [[21](#_ENREF_21)]. This is also called micropore or intracrystalline diffusion, as the structures are often three-dimensional. Diffusion in larger pores such that the diffusing molecule escapes from the surface field is referred to as macropore diffusion [[21](#_ENREF_21)]. The activation energy for diffusion can be calculated by studying the temperature dependence of the effective diffusivities, which can be modelled using the Arrhenius equation [[21](#_ENREF_21)]. Diffusion can be modelled according to Fick’s laws, in which the rate of transfer of a component through a mass-transfer area is proportional to the concentration gradient along the normal vector to that area [[21](#_ENREF_21)]. Adsorption kinetics have been modelled according to Fick’s laws of diffusion, but these can result in very complex mathematical functions, so other methods have been used in the literature. The linear driving force (LDF) model has arguably been the most used practical tool to analyse kinetics in heterogeneous solids for macroscopic, non-equilibrium diffusion experiments [[22](#_ENREF_22)].

In this work, the analysis was done on the recorded real-time kinetic data form volumetric gas sorption, which was fitted with the LDF model using the nonlinear fitting tool in the OriginPro 2018b software (OriginLab Corporation, Northampton, MA, USA), which is based on the Levenberg-Marquardt algorithm.

The LDF model was first introduced by Gleuckauf and Coates in 1947 to analyse chromatographic results [[23](#_ENREF_23), [24](#_ENREF_24)]. The integrated version of the LDF model is shown in Eq.1

(Eq.1)

where *t* is time, *n* *(t)* is amount adsorbed at time *t*, *n*2 is the equilibrium amount (for t →∞), *n*1 is the initial equilibrium uptake (for *t* = 0), *t*0 is the initial time (*t*= 0), and *k* is the lumped mass transfer coefficient (MTC) for the LDF model. In a volumetric experiment, as gas is introduced in the sample chamber the pressure will change due to adsorption of the gas by the sample as a function of time. The conditions of the experiment mean that there will be a changing concentration at the surface of the adsorbent particle, so a correction to the LDF must be made so that it can be adapted to volumetric experiments [[21](#_ENREF_21), [22](#_ENREF_22)]:

(Eq.2)

where Λ is the fraction of sorbate present that is adsorbed. This is calculated from the initial and final amounts in the bulk adsorptive, where *n*1b is the amount of adsorptive at *t =* 0 and *n2b* is the amount of adsorptive at equilibrium (*t → ∞)*:

(Eq.3)

From fitting the data, a lumped mass transfer coefficient (MTC) can be determined, which is then used to estimate the effective diffusivities at different temperatures. The temperature dependence of the effective diffusivities can be analysed with the Arrhenius equation to obtain the activation energy and the pre-exponential factor, which is related to the diffusion coefficient. We are aware that this is not a rigorous treatment of all the diffusional mechanisms of methane adsorption in these materials, and that there might be additional transport processes superimposed on intracrystalline diffusion. As it has been noted, in complex pore structures, more than one diffusional mechanism might be at play, but these can be very complex to model [[25](#_ENREF_25)] and, as noted above, there are experimental limitations that apply for a fast diffusing species in a volumetric (piezometric) experiment. Different methods exist to analyse adsorption kinetics, including methods based on Fick’s laws of diffusion, quadratic driving force models and pseudo-first order models [[22](#_ENREF_22), [26](#_ENREF_26)]. The authors used the linear driving force model since, as reported in the literature, it is simple, analytical and physically consistent [[22](#_ENREF_22)].

The effective intraparticle (also defined as the transport) diffusivities, can be calculated from the mass transfer coefficients assuming a spherical particle using Eq.4 [[23](#_ENREF_23), [24](#_ENREF_24)]:

(Eq.4)

where *k* is the mass transfer coefficient determined from the LDF fitting (in s-1), *D*ef the effective diffusivity (in m2 s-1), and *Rp* is the particle radius (in m). In our previous work, we determined the particle radius *R*p to be 3.55 µm for the AX-21 [[11](#_ENREF_11)], 5.57 µm for the MIL-101 (Cr) [[11](#_ENREF_11)] and 210 µm for the TE7 [[27](#_ENREF_27)], so effective diffusivities can be calculated directly from the determined LDF mass transfer coefficients.

With the effective diffusivities at different temperatures, the activation energy and the diffusion coefficient can be determined from fitting the data to the Arrhenius equation. The Arrhenius-type equation that relates the effective diffusivities and the activation energies is shown in Eq.5.

(Eq.5)

where *D*ef is the effective diffusivity in m2 s-1, *D*C is the pre-exponential factor in m2 s-1, *E*a is the micropore activation energy in kJ mol-1, *R* is the molar gas constant (8.314 x 10-3 kJ mol-1 K-1) and *T* is the temperature in K.

The LDF model was fitted to the kinetic data (Eq.2), with the initial time (*t*0) and initial amount (*n*1) fixed and the parameters *n*2 and Λ*k* extracted from the fitting. The uptakes *n*1 and *n*2 are determined in the instrument based on a mass balance on the sample cell. To calculate the mass transport coefficients *k* from Λ*k*, the fraction of adsorbate that is adsorbed needs to be calculated. Whereas the uptakes are determined in the instrument based on a mass balance done in the sample cell, the raw pressure readings from the transducer can be obtained and the adsorptive concentration in the bulk adsorptive of the sample cell can be calculated, for both initial (*n*1b) and equilibrium conditions (*n*2b). To obtain the available volume in the cell, the volume of the sample, calculated based on the dry mass basis and the skeletal volume was subtracted from the sample cell volume (1 cm3). The initial and final pressures in the cell were then used to calculate the initial (*n*1b) and equilibrium (*n*2b) amounts, using appropriate corrections to calculate the compressibility factors at those conditions of pressure and temperature. The dry masses of the samples were 153.2, 107.8 and 147.9 mg for the AX-21, MIL-101 (Cr) and TE7, respectively [[11](#_ENREF_11)]. With the initial and equilibrium number of moles, the fraction of gas in the adsorptive can be calculated for each step and the mass transfer coefficients can be corrected.

**Enthalpies of adsorption**

As discussed in the introduction, appropriate characterisation of the enthalpies is difficult, due to the difficulties of carrying out calorimetry in these systems, and the results are difficult to reconcile with other methods [[28](#_ENREF_28)]. The most commonly-used method for calculating enthalpies of adsorption is the isosteric method, which relies on the use of isotherms for the calculation [[29](#_ENREF_29)]. In the isosteric method, the temperature dependence of the isosteres (pressures at equal amounts adsorbed) is calculated and related to the enthalpies of adsorption. A convenient method is to use the Clausius-Clapeyron equation, which is derived from the exact thermodynamic equation for phase changes, which is the Clapeyron equation [[28](#_ENREF_28)]. We have previously compared the use of the Clapeyron, Clausius-Clapeyron and virial equation for the calculation of isosteric enthalpies in adsorbed hydrogen [[28](#_ENREF_28)]. In this work, we calculate the enthalpies of adsorption from the Clausius-Clapeyron method and compare the results obtained when using excess amounts and absolute amounts and, for the MIL-101 (Cr), we compare the isosteric enthalpies with differential scanning calorimetry, which is a direct method to measure enthalpies. Typical adsorption experiments can only yield excess amounts, as the adsorption has to be measured in a volumetric or gravimetric experiment, and this requires measurement of the void space available for adsorption. However, the excess amount (or the Gibbs surface excess, as is also designated) is a theoretical framework developed to facilitate the interpretation of adsorption, not a separate physical phase. In order to correctly assess the adsorption enthalpies, the amount of gas that is in an adsorbed phase has to be used in the calculations. The importance of using total amounts has also been highlighted by other authors when assessing enthalpies for natural gas in metal-organic frameworks, as well as the importance of the method of calculation [[30](#_ENREF_30)].

In the Clausius-Clapeyron equation, the isosteres are related to the enthalpy of adsorption, the molar gas constant and the temperatures. The Clausius-Clapeyron is a simplification of the Clapeyron equation, which assumes ideal gas behaviour and a negligible molar volume of the adsorbate. With these assumptions, the Clausius-Clapeyron equation can be written as in Eq.6.

(Eq.6)

where *P* is absolute pressure (in Pa), *T* is temperature in K, *n*a is amount adsorbed, *Q*stis the enthalpy of adsorption (in kJ mol-1), and *R* is the molar gas constant. The equation can be integrated, yielding Eq.7.

(Eq.7)

where the parameters are the same as in Eq.6 and *T*i and *T*f represent the initial and final temperatures. For more than two different temperatures, the isosteres can be plotted against 1/*RT*, and a linear fit through the isosteres at equal amounts adsorbed will have a slope that corresponds to the enthalpy of adsorption *Q*st.

The isosteric enthalpies obtained from both methods are compared with the zero-coverage enthalpy for the MIL-101 (Cr), which was measured on a high-pressure Differential Scanning Calorimeter (Setaram μDSC7 Evo), which was equipped with a high-pressure sample holder that is coupled to a Setaram Hy-Energy PCT-Pro 2000. Details for the measurement and calculation are included in Supporting Information. The instrument was recently used to measure enthalpies of adsorption of CO2 in MOF Cu-HKUST [[31](#_ENREF_31)].

**Results**

**Analysis of the kinetics**

Figure 1 shows methane adsorption isotherms in AX-21, MIL-101 (Cr) and TE7 from 250 K to 350 K and up to 14 MPa. These data were published in our previous work [[11](#_ENREF_11)].

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A)

B)

C)

Figure 1 – Excess methane isotherms for (A) AX-21, (B) MIL-101 (Cr) and (C) TE7 from 250 to 350 K and up to 14 MPa. Adapted from [[11](#_ENREF_11)].

The kinetic analysis was done at temperatures close to room temperature (300 K and 325 K) for all materials, and the points to analyse were equilibrium points 6 to 9 in each isotherm, so at equilibrium pressures ranging from ~0.33 to ~0.90 MPa for every material. This was to prevent issues associated with calculation of mass transfer coefficients, particularly thermal effects and dosing the gas to a chamber in conditions close to vacuum. The four kinetic points at 300 K for the AX-21 are shown in Figure 2.

Chart

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A)

B)

C)

D)

Chart

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**Figure 2 – Kinetic data for the AX-21 at 300 K with an equilibration pressure of (A) 0.33 MPa, (B) 0.48 MPa, (C) 0.66 MPa and (D) 0.85 MPa. Solid black dots are the experimental methane uptake points, the red line is the LDF fit and the blue line is the temperature (in K) in the sample cell. Insets in (A), (B), (C) and (D) are the same data zoomed in for the first 90 seconds.**

The other kinetic data that were analysed (AX-21 at 325 K, MIL-101 (Cr) at 300 and 325 K and the TE7 at 300 and 325 K) are included in Supplementary Information. As it can be seen in Figure 2, the temperature in the chamber is also in represented in the figure, so that thermal effects can be analysed. It can be seen from the figure that there is a tight temperature control in the sample cell, with a temperature change (< 0.5 K) upon opening of the valve. As noted previously, adsorption of methane can be highly exothermic, and the instrument allows for the temperature equilibration in the manifold, so this temperature change is most likely due to the exothermic nature of the process. It should also be noted that, at this macroscopic scale of hundreds of milligrams of material, it would be very difficult (if not impossible) to maintain complete isothermal conditions, as adsorption of methane is highly exothermic, which by definition means that there will be heat released upon adsorption, contributing to an increase in temperature. For the last kinetic point at 0.85 MPa, the temperature variation is slightly higher (~1 K) probably due to the higher gas uptake in this point. This larger temperature variation (~1 K) was also observed for the last point of the AX-21 at 325 K and for the last point of the MIL-101 (Cr) at both 300 and 325 K and again, this is likely due to higher amounts adsorbed. The TE7 showed a slightly higher temperature variation, with temperature differences of ~1 K for all of the points and temperature variation of ~2 K for the last point at 300 and 325 K. The higher temperatures seen in the TE7 are probably due to the higher heats being released upon adsorption, as TE7 has a higher enthalpy of adsorption at lower coverages than the other two materials, as noted in the enthalpies of adsorption section of this paper. The higher variations seen for the TE7 and its corresponding higher enthalpies of adsorption serve as further proof that the temperature variations are most likely due to the heats released upon adsorption and not due to thermal equilibration of the dosed gas.

The kinetic data was fitted with the LDF model and both the statistical coefficients (R2 > 0.986 for all the fits, with most of them having R2 > 0.994) and the figures show very good fits to data. The resolution of the data in the first points is critical for good fits to the model and, as noted in the introduction, the average time interval in the data for the first points is in the 0.5 second range. The initial section of the kinetic data, which corresponds to the step change in pressure and corresponding diffusion of methane onto the adsorption sites, is the most important for the estimation of parameters. After this initial period, the uptake remains constant, which is indicative of equilibrium. This is another reason why the Linear Driving Force Model is used, since the parameters are determined from this initial part of the kinetic data. The fact that the data is represented in Fig. 2 for longer periods does not influence the calculation of parameters. This means that, from Figure 2A, it would make minimal difference to the calculation of parameters if the data was fitted to 140 mins rather than the 160 mins represented in the figure. From the fits and using the fraction of adsorbate between the initial and final stages in each pressure step, the lumped mass transfer coefficients can be calculated. The lumped mass transfer coefficients can be related to the effective diffusivities using Eq.4, using the particle radius for each material. The average mass transfer coefficients, the standard deviation (SD) from the averages and the determined effective diffusivities for each material and each temperature are calculated and shown in Table 2.

**Table 2**. The average lumped mass transfer coefficients (MTC) and effective diffusivities (*D*eff) calculated from these using Eq. 4 at 300 and 325 K.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Material | AX-21 | | | MIL-101 (Cr) | | | TE7 | | |
| *T* /K | Average MTC /  min-1 | SD | *D*eff /  10-13 m2 s-1 | MTC /  min-1 | SD | *D*eff /  10-13 m2 s-1 | MTC /  min-1 | SD | *D*eff /  10-10 m2 s-1 |
| 300 | 12.80 | 3.19 | 1.79 | 16.50 | 4.00 | 5.69 | 16.18 | 3.79 | 7.93 |
| 325 | 16.05 | 4.01 | 2.25 | 20.53 | 5.80 | 7.08 | 19.12 | 3.98 | 9.36 |

The lumped mass transfer coefficients are shown in Figure 3. Some diffusion mechanisms, notably surface or micropore diffusivities, are thermally activated, and an activation energy can be calculated using the Arrhenius equation [[32](#_ENREF_32), [33](#_ENREF_33)]. The calculated effective diffusivities can then be analysed for temperature dependence using Eq.5, so the logarithm of the effective diffusivities is plotted against 1/*RT* and presented in Figure 3.



Figure 3 – Mass transfer coefficients from the linear driving force fits to the kinetic data for the AX-21, MIL-101 (Cr) and TE7 at 300 and 325 K (left). The temperature dependence of the effective diffusivities determined from the LDF for the AX-21, MIL-101 (Cr) and TE7 at 300 and 325 K (right).

The MTCs have very slight variations across the different pressure points and increase with temperature for all the materials, as would be expected. The effective diffusivities for AX-21 and MIL-101 (Cr) are in the same order of magnitude, ranging from 1.79 x 10-13 m2 s-1 for the AX-21 at 300 K to 7.08 x 10-13 m2 s-1 for the MIL-101 (Cr) at 325 K. It should be noted that, despite their different surface chemistry, the materials have similar BET surface areas (2550 m2 g-1 for the AX-21 and 2520 m2 g-1 for the MIL-101 (Cr)). The pore sizes that dominate their distributions are also somewhat similar, but the AX-21 has a much larger micropore volume and more porosity in the ultramicropore range (< 0.7 nm). It should also be noted that the particle sizes used for both materials in this study are in the same order of magnitude (3.55 and 5.57 µm for the AX-21 and MIL-101 (Cr), respectively. The TE-7 has effective diffusivities that are larger than the ones calculated for AX-21 and MIL-101 (Cr). The material has a much lower BET surface area, a smaller micropore volume, and pores in the micro and macropore region. It should also be noted that the particle sizes of the TE7 beads are much larger than the particle sizes of the other two materials. Methane adsorbs in narrow micropores in high surface area carbons [[34](#_ENREF_34)] and the larger effective diffusivities seen in TE7 might be due to its smaller surface area (hence smaller amount of adsorption sites), narrow microporosity and a fraction of macropores, which might increase diffusion of methane to adsorption sites. The calculated values are comparable to those obtained by Rufford et al. for adsorption of methane in activated carbon Norit RB3 at 302.3 K from 106 kPa to 900 kPa, which ranged from 3.2 to 0.3 min-1 [[35](#_ENREF_35)]. The values for effective diffusivities are also in the range of other reported methane diffusivities, which were in the order of 1 to 2 x 10-9 m2 s-1 for MOF-5 and MOF-177 and 5.65 x 10-11 m2 s-1for zeolite 5A [[36](#_ENREF_36)]. Ribeiro et al. reported values of 3.00, 5.50 and 8.00 x 10-11 m2 s‑1 for the effective diffusivities of methane at 303, 323 and 343 K in activated carbon honeycomb monoliths [[37](#_ENREF_37)]. Another study by Bao et al. [[38](#_ENREF_38)] investigated diffusion of methane in magnesium metal-organic framework Mg-MOF-74 in temperatures close to the temperatures in our study (278, 298 and 318 K) and obtained similar values for effective diffusivities (in the range of 10-12 m2 s-1) and similar activation energies (1.7 kJ mol-1). Saha et al. [[36](#_ENREF_36)] investigated methane adsorption in MOF-5, MOF-177 and Zeolite 5A and obtained effective diffusivities ranging between 1.82 x 10-9 m2 s-1 in MOF-5 and 5.65 x 10-11 m2 s-1 for zeolite 5A at 298 K.

The solid curves in Figure 3 represents the linear fit through the points and, as seen in Eq. 5, the slope of the linear curve fit is equal to *E*a, which is the activation energy for diffusion. The activation energies and diffusion coefficients determined from the linear fits to the data in Figure 3 are presented in Table 3.

**Table 3**. The activation energies and diffusion coefficients determined from the Arrhenius equation applied to the effective diffusivities.

|  |  |  |  |
| --- | --- | --- | --- |
| Material | AX-21 | MIL-101 (Cr) | TE7 |
| Activation energy /  kJ mol-1 | 7.42 | 7.09 | 5.38 |
| Diffusion coefficient *D*c /  m2 s-1 | 3.50 x 10-12 | 9.75 x 10-12 | 6.84 x 10-9 |

Other authors have also studied the temperature dependence of the effective diffusivities and mass transfer coefficients of methane in porous materials using the Arrhenius equation. Rufford et al. studied the temperature dependence of the mass transfer coefficients in methane adsorption in activated carbon Norit RB3 and obtained a value of 9.66 kJ mol-1 for the activation energy [[35](#_ENREF_35)]. Ribeiro looked at the adsorption of methane in activated carbon honeycomb monoliths [[37](#_ENREF_37)], and calculated diffusion coefficients from fitting diluted breakthrough data to a mathematical model that assumes diffusion in a single channel of the monolith. The temperature dependence of the diffusion coefficients was then analysed, yielding an activation energy of 19.5 kJ mol-1, a value that is higher than the ones reported in this work. As noted above, the honeycomb monolith displayed effective diffusivities in a slightly higher range to the ones obtained in our study (3.00 - 8.00 x 10-11 m2 s-1). Yang et al. studied methane adsorption in the carbon molecular sieve (CMS) 131510 and obtained values of 39.27 kJ mol-1 and 44.26 kJ mol-1 for the micropore diffusivity and the barrier mass-transfer coefficient, respectively [[39](#_ENREF_39)]. Again, these values are higher than the activation energies reported here, but it should be noted the different packing formats of the materials analysed in this report (powders and beads), in comparison with the values reported for monoliths.

**Enthalpies of adsorption**

In order to extract enthalpies of methane adsorption form the gas uptake data, we have calculated the isosteres (pressures at equal amounts adsorbed) at 1, 2, 4, 6 and 8 wt.% (dry mass basis) for the three materials at temperatures from 250 K to 350 K. In our analysis, the isosteres for equal amounts adsorbed were determined from the interpolate function in OriginPro. The logarithm of the determined values was then plotted against 1/*RT* and the results are shown in Figure 4. A linear fit was done for all equal amounts adsorbed, yielding the enthalpies of adsorption, which are shown in panel d).



C)

D)

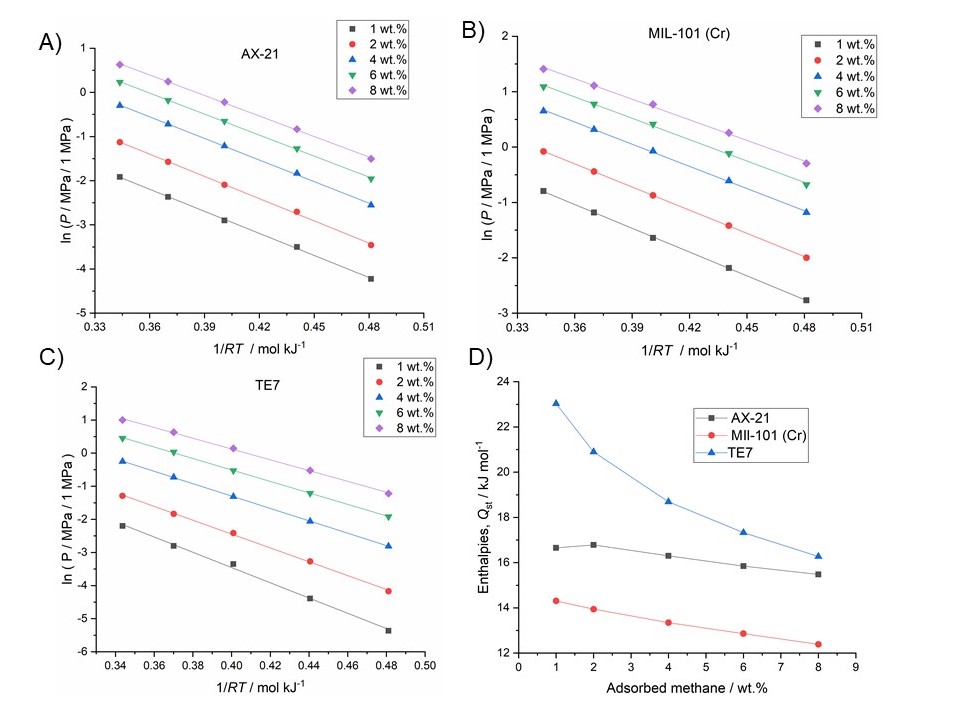
A)

B)

Figure 4 – The isosteres and linear fits for the (A) AX-21, (B) MIL-101 (Cr) and (C) TE7 determined from the excess isotherm. The values that correspond to the gradient of the curve (the isosteric enthalpies) are plotted in (D) for the three materials.

As it can be seen from Figure 4, the enthalpies were determined for the three materials as a function of coverage. The shape of the enthalpies is expected, with higher enthalpies associated to the lower coverage, and a decrease in values with increasing coverage. The MIL-101 (Cr) has the lowest enthalpies of all of the materials, with values ranging from 16 to 14 kJ mol‑1 for coverages up to 8 wt.%. The activated carbons AX-21 and TE7 have higher enthalpies, with the AX-21 having enthalpies ranging from 18 to 16 kJ mol-1 and the TE7 showing an enthalpy of 21 kJ mol-1 at 1 wt.%. These values are in comparable ranges to other enthalpies calculated for these materials, with metal-organic frameworks having reported values of 12 kJ mol-1 for MOF-5, and other MOFs such as HKUST-1, PCN-14, and Ni(dobdc) showing values between 17 and 22 kJ mol-1 [[30](#_ENREF_30)]. AX‑21 was also reported in the same study as having an enthalpy ranging from 16 and 12 kJ mol‑1, with all of these values calculated using single- and dual-site Langmuir models [[30](#_ENREF_30)]. It has been shown by Bhatia and Myers that the optimum storage temperature for storage and delivery of methane at 3 and 0.15 MPa is 254 K, and the optimum adsorption enthalpy is 18.8 kJ mol-1 [[40](#_ENREF_40)]. Also, it should be noted that the enthalpy of vaporisation of methane is a function of the temperature and is approximately 8.6 kJ mol-1 at 111 K.

However, as previously discussed, the excess does not represent the true quantity of gas adsorbed in the pore and does not have any physical meaning, so it does not make much sense to calculate the adsorption enthalpy using the excess quantity, as it is not the enthalpy that corresponds to the phase change between bulk and adsorbed state. In our previous work, we have introduced a methodology that distinguishes between excess, absolute and total amounts [[41-43](#_ENREF_41)]. In our theoretical framework, the excess is the amount measured experimentally, the absolute amount represents the quantity in the adsorbed phase in the pore (*i.e.* in a different, denser phase) and the total is the absolute amount plus the amount of bulk gas present in the pore. Using this methodology to analyse different materials, we have obtained very high densities for adsorbed hydrogen in activated carbon, which were confirmed experimentally using inelastic neutron scattering [[44](#_ENREF_44)]. As the absolute amount is the amount that represents that gas that is in a different phase, this is the amount that should be used for the enthalpy calculations. For this reason, we calculated the isosteric enthalpies from the absolute amounts. The fitting to the absolute amounts used the same methodology we have previously reported with the Tóth equation [[45](#_ENREF_45)], with each isotherm fitted with the model and the parameters that define the adsorbed phase density, the heterogeneity factor *c* and the affinity parameter *b* extracted from the nonlinear fits. The pore volume was fixed in each fit, and the value determined experimentally from the Dubinin-Radushkevich method was used, which is equal to 1.97 cm3 g-1 for the AX-21, 0.81 cm3 g-1 for the MIL-101 (Cr) and 0.52 cm3 g-1 for the TE7. These parameters are sufficient to define an absolute isotherm for each temperature. The fits were presented in our previous work [[11](#_ENREF_11)]. Using the parameters, the isosteres were determined from the absolute amounts using the interpolation tool in OriginPro, and the same methodology used for the excess (the Clausius-Clapeyron method) and the same equation (Eq.7) were used to calculate the enthalpies, to enable the direct comparison between the methods. The logarithm of the isosteres of the absolute amounts was plotted against 1/*RT* and shown in Figure 5. As in Figure 4, a linear fit was done for all equal amounts adsorbed, and the gradient of the curve is equal to *Qst*. The enthalpies of adsorption are shown in panel d) in Figure 5.



C)

D)

B)

A)

Figure 5 – The isosteres and linear fits for (A)AX-21, (B) MIL-101 (Cr) and (C) TE7 determined from the absolute isotherm. The values that correspond to the gradient of the curve (the isosteric enthalpies) are plotted in (D) for the three materials.

The isosteric enthalpies determined from the absolute amounts show that the MIL-101 (Cr) still has the lowest enthalpies, and also shows little variation between enthalpies at lower coverages which are around 14 kJ mol-1, down to little over 12 kJ mol-1 for 8 wt.%. The AX-21 isosteric enthalpies also do not show much variation, with even a slight increase in enthalpies from 1 to 2 wt.% at around 17 kJ mol-1, and a slight decrease in values up to 8 wt.%. These are not very significant differences in values and could be explained by the fact that AX-21 is a high-surface area carbon with a lower degree of surface heterogeneity. Finally, the highest values and variation for the enthalpies are seen in the TE7, which shows an enthalpy of 23 kJ mol-1 at 1 wt.% and a rapid decrease to 17 kJ mol-1 at 8 wt.%. The higher enthalpies in the activated carbons might be related to their bigger proportion of micropores, especially ultramicropores (<0.7 nm). In this respect, even though TE7 has a lower surface area, it has most of the porosity in the ultramicropore range, almost no porosity between 2 and 20 nm and some pores in the macropore range. The AX-21 has a significant percentage of pores in the ultramicropore range but the highest percentage of pores are between 1 and 3 nm. This larger percentage of bigger pores in AX-21 might explain the lower enthalpies of adsorption in AX-21 when comparing with TE7.

The enthalpies obtained from both methods were then compared, as shown in Figure 6.



Figure 6 – The isosteric enthalpies determined from the absolute (solid line) and excess (dotted line) for the AX-21, MIL-101 (Cr) and the TE7. The horizontal red line corresponds to the zero-coverage enthalpy measured from DSC for the MIL-101 (Cr) at 300 K

As seen in Figure 6, it is difficult to discern a pattern for the comparison between the enthalpies determined from the absolute and the excess quantities. For the TE7, the enthalpies calculated from the absolute have a higher value at low coverage, with the values having similar values at 4 wt.% and the absolute showing smaller enthalpies at higher coverages. For the AX-21, the values obtained from both the excess and absolute amounts are quite comparable, in both profile and magnitude, with a small difference at 1 wt.% coverage, where the amounts determined from the excess have a ~1 kJ mol-1 difference. For this material, the enthalpies from the excess amount are also always slightly higher than the enthalpies determined from the absolute amounts. Finally, the enthalpies calculated for the MIL-101 (Cr) show some difference, with again the enthalpies determined from the excess showing higher values than the values determined from the absolute amounts. This difference is slightly more pronounced at lower coverages (almost 2 kJ mol-1 at 1 wt.%) and at higher coverages (around 1.5 kJ mol-1 at 8 wt.%). The zero-coverage enthalpy for MIL 101 was also directly measured via DSC (through integration of the first exothermic peak in Figure S6). Only the zero-coverage enthalpy is calculated, because this is the adsorption heat that is related to the first layer of adsorbate on the solid, with interactions at higher pressures becoming more difficult to measure and correlate with other methods. The value obtained for the zero-coverage enthalpy measured from the DSC at 300 K (19.6 kJ mol-1) was also higher than the values calculated from the absolute (16 kJ mol-1) and excess (14 kJ mol-1) , suggesting that there are still some issues to address when trying to reconcile direct methods such as DSC with indirect ones such as the isosteric method, as the differences are quite significant. Other authors have also investigated adsorption calorimetry in methane experiments. Deng et al. [[46](#_ENREF_46)] investigated methane adsorption in anthracite and aimed to compare calorimetry heats with the ones obtained through the isosteric method. The values reported from calorimetry ranged from 22.49 to 28.47 kJ mol-1. The authors attributed the differences from the calorimetry to the isosteric heats on the calculation methods, including the use of the virial equation and the Clausius-Clapeyron, whereas our study focusses on the use of the absolute and excess quantities. Wu et al. [[47](#_ENREF_47)] measured methane adsorption in MOF HKUST-1using a microcalorimeter and measured a differential enthalpy of adsorption of 21.1 kJ mol-1 at 25 °C. Recently, Moreno-Pirajan and Giraldo [[48](#_ENREF_48)] also looked at methane adsorption in five different MOFs (ZIF-8, HKUST-1, IRMOF-1, MOF-177 and Mg-MOF-74), looking at calorimetry and enthalpies calculated using different methods, including the Dubinin-Astakhov, Tóth, Clausius-Clapeyron and UNILAN. The calorimetry heats are the highest in all materials, with reported values of 30.00 kJ mol-1 for the Mg-MOF-74, 25.00 kJ mol-1 for MOF-177, 17.45 kJ mol-1 for IRMOF-1, 12.50 kJ mol-1 for HKUST-1 and 9.95 for ZIF-8. We have obtained a comparable value at zero-coverage for MIL-101 (Cr), which is 19.6 kJ mol-1.

This figure shows that, for the materials considered, there are slight differences between calculating the enthalpies from the absolute and excess amounts, and that both under- and overestimations of the enthalpies can occur if the enthalpies are calculated based only on excess amounts. This can represent variations of up to 10%, so it is recommended that isosteric enthalpies should be calculated using the absolute amounts, as these represent large changes in amounts of heat released upon adsorption. Ensuring proper determination of the enthalpies of adsorption is critical for the heat management in adsorbed methane storage systems, as amounts adsorbed are very temperature dependent, and a rigorous treatment of the enthalpies can help in the design of storage systems with better heat and temperature control.

**Conclusions**

Methane storage in porous materials is a valid alternative for increasing energy densities in mobile applications. Some materials are close to meeting the targets proposed by the US Department of Energy, but challenges remain. In this work, we have analysed kinetic data for the adsorption of methane in highly porous materials using the linear driving force model (LDF). The results show that the model fits well to the available kinetic data and lumped mass transfer coefficients extracted from the fits of the LDF to the data range from 9.2 to 25.4 min-1, with the average coefficients showing values between 12.8 and 20.5 min-1. The effective diffusivities extracted for the materials range from 1.79 x 10-13 m2 s-1 for the AX-21 at 300 K to 9.36 x 10-10 m2 s-1 for the TE7 at 325 K. The diffusivities and mass transfer coefficients were also investigated for temperature dependence and the activation energies were determined. The activation energies were calculated as 7.415, 7.086 and 5.375 kJ mol-1 for the AX-21, MIL-101 (Cr) and TE7, respectively. The enthalpies of adsorption were also investigated, with the enthalpies calculated using the Clausius-Clapeyron method using both excess and absolute amounts. The values show that there is some discrepancy when using the different amounts, and the enthalpies can be either under- or overestimated for up to 2 kJ mol-1 depending on the materials, which represents variations of around 10%. For the MIL-101 (Cr), the values are still lower than the values obtained from differential scanning calorimetry, with a difference of around 3.5 kJ mol-1 for the zero-coverage enthalpy and the low coverage obtained by the isosteric method. This difference is significant, and further underlines the importance of refining these methods to try and bridge the gap between direct methods such as calorimetry and indirect methods such as the isosteric method.

**Supporting Information**

The Supporting information includes further experimental details on the kinetic data and the remaining fits to kinetic data with the LDF model, and the details on the differential scanning calorimetry experiments and analysis.

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