Methane preconcentration by adsorption: a methodology for materials and conditions selection

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Abstract Methane (CH₄) adsorption has been widely studied, mainly in the context of natural gas purification. A much less prominent, but highly relevant application is the preconcentration of CH₄ from ambient air. In this study, we compare six different commercial adsorbent materials with respect to their effectiveness for methane preconcentration: a macroporous polymeric resin (HayeSep D), multi-walled carbon nanotubes, two microporous metal-organic frameworks (HKUST-1 and ZIF-8), and two zeolites (5A and 13X). The most relevant properties, such as isosteric enthalpy of adsorption, specific surface area and the selectivity for CH₄ adsorption over N₂ were characterized by analyzing adsorption/desorption isotherms. Using these parameters, we discuss the tested adsorbents with respect to the most important properties and identify the most promising candidates. Furthermore we identify the experimental conditions that are expected to give the best results with respect to practical applications.

Keywords Methane · Adsorption · Isosteric enthalpy · Gas selectivity · Specific surface area · Preconcentration

1 Introduction

Global warming resulting from anthropogenically emitted greenhouse gases (GHGs) is an important environmental issue. After CO₂, methane (CH₄) has the highest contribution to the greenhouse effect and on a per-molecule basis, its global warming potential is 25 times higher compared to CO₂ on a 100 year timescale (Solomon 2007). Global CH₄ emissions are relatively well quantified, but the strength of the individual source components and their trends are not (Solomon 2007). By measuring the stable isotopic composition of CH₄ in ambient air with high accuracy (≈1 ppt = 10⁻¹² mol/mol), the major source processes can be identified. The standard way to achieve such measurements is isotope-ratio mass-spectrometry, which is generally laboratory-based (Werner and Brand 2001). However, recently developed infrared laser-based measuring systems are an attractive alternative, especially for field measurements. Such field measurements based on laser spectroscopy have been shown to yield reliable results at high temporal resolution for the stable isotopes of CO₂ (Tuzson et al. 2008, 2011). However, for the less abundant GHGs, such as N₂O and CH₄, preconcentration of the target species is required (Mohn et al. 2010, 2012) to reach a precision of 0.1 % for the ratio of the isotopologues. Otherwise analysis is limited to source studies at high mixing ratios (Wunderlin et al. 2012, 2013; Koester et al. 2013). An efficient way for methane preconcentration is achieved by performing temperature cycles on suitable adsorbent materials (Bock et al. 2010). For continuous monitoring of CH₄ isotopologues in ambient air under field conditions, temperatures that do not require the use of liquid nitrogen are preferred.

High-precision laser spectroscopy by mid-infrared absorption comprises the usage of multipass absorption cells with a volume of up to one liter, generally at 1–10 kPa...
The best spectroscopic precision is typically obtained at CH$_4$ mixing ratios of several hundred ppm. This implies the preconcentration by a factor $>100$, given typical ambient mixing ratios of 1.8 ppm. For adsorptive preconcentration, it is necessary to use an adsorbent material with high CH$_4$ adsorption capacity, i.e., high specific surface area, and a high selectivity for CH$_4$ over N$_2$. Selectivity for CO$_2$ and H$_2$O is less important because these components can be quantitatively removed with a typical pretreatment (Mohn et al. 2010; Bock et al. 2010). Additionally, quantitative adsorption/desorption of the analyte is required to avoid kinetic isotopic fractionation effects due to subtle but characteristic differences in the enthalpy of adsorption of individual CH$_4$ isotopologues (Phillips and Hook 1967; Fayet et al. 1990). The most frequently used preconcentration adsorbents for CH$_4$, N$_2$O and volatile organic compounds (VOC) are HayeSep polymers (Mohn et al. 2010; Bock et al. 2010; Reimann et al. 2008) and carbon-based materials (Thammakhet et al. 2005; Saridara et al. 2010; Wu et al. 2003; Wong et al. 2013; Dettmer and Engewald 2002; Falkovich and Rudich 2001; Li et al. 2012). Recently, multiwalled carbon nanotubes (MWCNT) were reported to yield the highest uptake of a selection of carbon-based adsorbents (Saridara et al. 2010). Porous zeolites may also be a valuable alternative, because of their high surface area and high potential selectivity due to the molecular sieve effect (Yaremiv et al. 2013; Delgado et al. 2013; Wang et al. 1998). For example, molecular sieves have been shown to be appealing for the application of CO$_2$/CH$_4$ separation (Lu et al. 2013). More recently, a different class of adsorbent materials known as metal-organic frameworks (MOFs), which exhibit exceptionally large specific surface areas, has shown to be highly promising for applications in gas storage and gas separation (Li et al. 1999, 2009; Mendoza-Cortes 2010; Dren et al. 2004; Wu 2010; Moellmer et al. 2011). Using adsorbents under material-specific optimal conditions for selective CH$_4$ adsorption may greatly increase the performance of applications such as preconcentration of CH$_4$ from ambient air for laser spectroscopic analysis.

In this study, a selection of six promising commercially available adsorbents are compared regarding CH$_4$ adsorption amount, CH$_4$/N$_2$ selectivity and isosteric enthalpy: a macroporous polymeric resin (HayeSep D), MWCNT, two microporous metal-organic frameworks (HKUST-1 and ZIF-8), and two zeolites (5A and 13X). Adsorption measurements of CH$_4$ and N$_2$ at four temperatures between 77 and 296 K were performed. The specific surface area was determined using N$_2$ and CH$_4$ adsorption isotherms at 77 K, and the isosteric enthalpy was calculated using a model-independent method. This is to our knowledge the first systematic investigation of such a variety of different adsorbent materials for CH$_4$ with the aim of finding a material that is suitable for analytical applications.

### 2 Materials and methods

The investigated materials were obtained from the following sources: HayeSep D (100/120 mesh), the MOFs HKUST-1 (D50 15.96 μm) and ZIF-8 (D50 4.9 μm), as well as the zeolites Z5A and Z13X (both 100/120 mesh) from Sigma Aldrich (Switzerland). The MWCNT (~95%, < 8 nm) were purchased from Cheap Tubes Inc (USA). All adsorption measurements were performed with a Belsope Max (BEL Inc., Japan) volumetric Sieverts apparatus. Methane and nitrogen gas were obtained from Messer AG (Switzerland), with purities of 99.995 and 99.9999 %, respectively.

During experiments, approximately 500 mg samples were held in a stable cold bath at temperatures of 296, 273, 196 and 77 K (±0.2 K), corresponding to room temperature, ice water, dry ice and liquid nitrogen, respectively. Adsorption measurements were performed between 0 and 100 kPa and followed by desorption measurement at each temperature. For methane adsorption measurements at 77 K the pressure range was set to 0–1.8 kPa and desorption measurements were not possible, probably because the methane froze on the surface of the adsorbents. The accuracy of the volumetric Sieverts apparatus is determined by the resolution of the pressure gauge, among other factors. The overall uncertainty of an individual data point is approximately ±0.015 mmol/g upon repeated measurements.

### 3 Analysis

To determine the most suitable material for CH$_4$ preconcentration, specific uptake, selectivity and isosteric enthalpy of adsorption should ideally be investigated in a wide range of temperature and pressure. The relevant parameters may then be extracted from the measured isotherms and estimated for practical working conditions in the scheduled application. For this analysis, a fitting equation and/or model is necessary to interpolate the data. In the following sections, we briefly outline the methods used.

#### 3.1 Adsorption models

The Langmuir model is the simplest model of physical adsorption of gas on a surface, beyond Henry’s law. It is useful for adsorption systems where the mechanism is monolayer-like and the adsorption sites are relatively homogeneous since only one binding energy is used. At low temperatures and on specific adsorbents where multiple layers cannot easily exist, it provides a good quality of fit to adsorption data and the isosteric enthalpy and specific surface area can be readily obtained (Gregg and Sing 1991).
The Brunauer–Emmett–Teller (BET) model is an extension of the Langmuir model which allows for multilayer formation where the binding energy of sites in the second layer and higher is set equal to the heat of liquefaction. Beyond the initial point of multilayer formation (referred to as Point B), adsorption proceeds nearly linearly with respect to pressure, and the specific surface area of the adsorbent can thus readily be determined. This model is useful for characterizing a wide variety of sorbents at low temperature (usually with N2 at 77 K) and although the limitations of this method have been widely discussed, it remains in common use due to its simplicity (Sing 2001). For the purpose of this study, the low temperature adsorption measurements (77 K) were analyzed with both the Langmuir and the BET model to deduce adsorption surface areas. The quality of fit of both models is evaluated based on the residual of the fit given in the Online Resource.

However, adsorption models which can account for phenomena at higher temperatures and pressures are more complicated, as has been previously discussed in great detail (e.g., Bimbo et al. 2011). The data in this study were fitted, for example, with a generalized Langmuir type equation which can account for adsorption on heterogeneous surfaces. Though fits with even larger numbers of fitting parameters were attempted, the range of temperatures and pressures measured in this study were not conducive to its practical use. A common method for fitting adsorption data over a large range of temperature is to use a virial-type equation (1) (Czepirski and Jagiello 1989; Stadie 2012). This model-less approach is beneficial in that it relies on relatively few fitting parameters and retains a very simple expression for the isosteric enthalpy of adsorption.

\[
\ln\left(\frac{p}{n}\right) = \frac{1}{T} \sum_{i} a_{i}n_{i} + \sum_{i} b_{i}n_{i}^{2}
\]

where \(n\) is the molar amount of gas adsorbed per unit weight, \(p\) is the equilibrium pressure, \(T\) the temperature and \(a_{i}\) and \(b_{i}\) are the Virial coefficients of order \(i\). From this formula, the isosteric enthalpy is found by employing the Clausius–Clapeyron relation (2) (Stadie et al. 2013).

\[
-H_{\text{ads}} = R \left( \frac{\partial \ln p}{\partial (1/T)} \right)_{n} = R \sum_{i} a_{i}n_{i}^{i}
\]

The temperature dependence of the isosteric enthalpy is not accessible in this method, and the pressure dependence is known to be susceptible to various pitfalls. For this reason, we focus on the value in the Henry’s law limit \((p \to 0)\) (3).

\[
-H_{0} = R \lim_{n \to 0} \sum_{i} a_{i}n_{i}^{i} = R\delta_{0}
\]

The simplest approach, for comparison purposes, is to fit the adsorption data using a linear interpolation method and applying the simplified Clausius–Clapeyron equation (4).

\[
\ln(p) = -\frac{\Delta H_{\text{ads}}}{RT} + \epsilon
\]

where \(R\) is the molar gas constant and \(\epsilon\) is a constant. This is often unreliable for obtaining anything except an approximation of the isosteric enthalpy of adsorption (the Henry’s law value) via the Clausius–Clapeyron equation and relies on large numbers of data points to be successful (Stadie 2012).

Once a fitting equation has been selected, the adsorptive selectivity between two gas species can also be estimated using gas uptake data. In this study, we focus on estimating the selectivity in two ways defined by the parameters \(X\) and \(Y\).

\[
X = \frac{n_{\text{CH}_4}(p, T)}{n_{\text{N}_2}(p, T)}
\]

\[
Y = \frac{\Delta H_{\text{ads}}^{\text{CH}_4}}{\Delta H_{\text{ads}}^{\text{N}_2}}(p = 0, T)
\]

Parameter \(X\) is the ratio of adsorption uptake of \(\text{CH}_4\) and \(\text{N}_2\) under identical conditions and \(Y\) is the ratio of the \(\Delta H_{\text{ads}}\) for \(\text{CH}_4\) and \(\text{N}_2\). The interpretation of these coefficients will be discussed in detail in Sect. 4.4.

4 Results and discussion

From a phenomenological point of view, there is a considerable difference between the adsorption of gases at near ambient temperatures (above 196 K) and cryogenic temperature (77 K), where effects due to a nearly fully covered surface have to be taken into account. Therefore, we have chosen to focus on the temperature range of 196–296 K to determine isosteric enthalpy and selectivity, while the specific surface area was determined from the data measured at 77 K. With these important parameters, we discuss the possible application of the evaluated materials for preconcentration.

4.1 Adsorption of \(\text{CH}_4\) and \(\text{N}_2\) in the temperature range of 196–296 K

At temperatures 196, 273 and 296 K, all of the adsorbents exhibit Type I behavior with respect to \(\text{N}_2\) and \(\text{CH}_4\) adsorption (Gregg and Sing 1991). In this temperature region the best global fit of adsorption data was obtained using the model-less virial approach in second order. Information on the model selection and the residual of the fits are given in the Online Resource. In Figs. 1, 2, 3, 4, 5, 6 the measured \(\text{CH}_4\) and \(\text{N}_2\) adsorption (closed symbols) and desorption isotherms (open symbols) are given. Based on
the excellent agreement of adsorption and desorption measurements significant hysteresis effects can be excluded. The highest adsorption capacity for CH₄ and N₂ in the temperature range of 196–296 K was observed for HKUST-1. The zeolites exhibit a high adsorption capacity of CH₄ especially at low pressures (<10 kPa), but the difference in adsorption capacity of CH₄ and N₂ is significantly smaller than for the other candidate materials in this study.

4.2 Isosteric enthalpy of adsorption

From the extracted fit coefficients, the isosteric enthalpy at zero adsorption amount (\( \Delta H_0 \)) was determined using (3). Additionally, the isosteric enthalpy was calculated by a linear interpolation method at low adsorption amount and using (4). The results are presented in Table 1 and show that Z5A and HayeSep D have the highest enthalpy of methane adsorption while ZIF-8 exhibits the lowest (Fig. 7). For N₂ the molecular sieves showed the highest
enthalpy of adsorption and ZIF-8 the lowest. This will be discussed in more detail in Sect. 4.4. In Table 1, the $\Delta H_0$ values calculated by the linear interpolation method are compared with those from the virial method.

4.3 Surface area

Figures 8 and 9 show the $N_2$ and $CH_4$ adsorption isotherms of the candidate materials at 77 K. The data were fitted with both the Langmuir and the BET model, and the surface area was calculated according to convention (Gregg and Sing 1991). The shape of the $CH_4$ isotherms are very similar to those of $N_2$, except that the saturation pressure is lower for $CH_4$. For $N_2$ the occupied surface area per molecule was taken to be 0.162 nm$^2$ (Gregg and Sing 1991) and 0.1918 nm$^2$ for $CH_4$ (Chaix et al. 1996). The Langmuir model has a better agreement with the $N_2$ adsorption isotherms for the MOFs and the zeolites, presumably because of their monolayer-like adsorption behavior due to very narrow pores. For HayeSep D and MWCNT the $N_2$ and $CH_4$ adsorption curves show a multilayer behavior with a linear uptake according to Henry’s law above $P_a$; thus the BET-model is more suitable. This behavior can be rationalized by the macroporous structure of these materials. Table 1 shows the surface areas of materials calculated using the BET and the Langmuir method for both adsorbates. To indicate limited agreement between the experimental data and the model fit, some values are given in parentheses (see Online Resource for more information).

The MOFs exhibit by far the highest surface of 1450–1700 m$^2$/g. MWCNT, on the other hand, show a relatively low surface area of 350–500 m$^2$/g.

4.4 Selectivity

Mixing ratios of $CH_4$ in background air are less than 2 ppm, compared to around 78% for $N_2$. In order to efficiently preconcentrate $CH_4$ to levels suitable for analysis, it is important that the adsorptive properties of the chosen adsorbent are largely superior for $CH_4$ over $N_2$. Thus, the adsorptive selectivity of $CH_4$ is perhaps the most important criterion for selection of an adsorbent for this purpose. This selectivity can be determined in several ways. A simplified and conventional approach is to compare $CH_4$ and $N_2$...
adsorption capacity, determined in separate experiments but under identical conditions (Wiersum et al. 2013). For example, selectivities of various MOFs and other materials for different gas compounds have been investigated by comparing the equilibrium adsorption capacity at specific conditions (Li et al. 2009; Pawar et al. 2009). In cation–exchanged zeolite mordenite and MOFs, selective properties have been quantified by taking the ratio of the Henry’s constants or comparing the isosteric enthalpy of adsorption of each gas (Peter et al. 2005; Liu et al. 2008; Moellmer et al. 2012). More sophisticated methods of measuring the selectivity of CH$_4$ adsorption over N$_2$ adsorption are also reported, for example breakthrough measurements, however these experiments are tailored to specific process conditions and require elaborate experimental apparatus beyond the scope of this study.

In this study, we focus on estimating the selectivity in two ways defined by the parameters $X$ and $Y$, which are given by Eq. (5) and (6). As mentioned before, both values are mainly discussed for a comparative assessment of candidate adsorbents. Variable $X$ gives the ratio of the binding energy of a distinct adsorbent for CH$_4$ in relation to N$_2$ gas. Variable $Y$ stands for the ratio of capacity at 196 K and 100 kPa for CH$_4$ relative to N$_2$. This value is particularly interesting, as it represents the selectivity near the saturation point, where Henry’s law is less dominant. The respective ratios $X$ and $Y$ are given in Table 1, which reveals that both approaches are in good agreement. HayeSep D and ZIF-8 show the most promising properties in terms of selectivity. Due to its weaker $\Delta H_{ads}$, one must consider, however, that ZIF-8 is not saturated at 100 kPa for either gas component and thus the ratio of adsorption of CH$_4$ and N$_2$ in this pressure range is not fully comparable to the other materials. This means that the value of $Y$ is more significant for ZIF-8 in terms of selectivity and, thus, HayeSep D shows the best selectivity of all materials, followed by ZIF-8, HKUST-1 and MWCNT. A similar conclusion can be drawn from Fig. 11, where the adsorption ratio has been calculated continuously in the range of 0–100 kPa and 200–300 K using the virial equation fits. While one must exercise caution when interpolating the data taken from only three isotherms, Fig. 11 is meant to show a qualitative comparison of the effects of temperature and pressure on the selectivity of each material. There are two main conclusions drawn from this plot. First, HayeSep D offers the most promising selective properties under most conditions while the molecular sieves show the least, which is consistent with the information derived from the isosteric enthalpy of adsorption for CH$_4$ and N$_2$. Secondly, the selective behavior of the adsorbents studied is more or less constant in the analyzed temperature and pressure regime, with one exception: namely, HayeSep D at low pressures and temperatures. In this region, HayeSep D exhibits an enhanced selectivity compared to the other candidate materials which can be directly evidenced in the measured isotherms at 196 K. Zeolites 5A and 13X exhibit a low selectivity, with $\Delta H_{ads}$ being higher for N$_2$ than for CH$_4$, which excludes them from being suitable candidates for this application.

4.5 Temperature behavior

To optimize the effectiveness of a preconcentration unit, it is important to find the ideal regime where selectivity and
adsorption capacity are optimized for both adsorption, and desorption conditions. Such optimization processes have been useful in other reported applications (Wurzbacher et al. 2011; Harpalani 2006). For example, thermogravi-metric measurements on functionalized silica-gel were fitted to isotherm models and the results successfully applied to predict desorption capacities and optimize a temperature-vacuum swing process to capture CO$_2$ (Wurzbacher et al. 2011). Using the fitted isotherm data, it is possible to construct new isotherms within the regime measured to identify the best temperature ranges for obtaining maximum adsorption capacity and rapid desorption. Figure 10 shows the CH$_4$ adsorption isotherms of all adsorbent materials as a function of pressure and temperature; temperatures below 200 K are found to be most promising because the adsorption capacity increases considerably with decreasing temperature, while the CH$_4$/N$_2$ selectivity increases or stays more or less constant (Fig. 11). This is particularly noticeable in the low pressure regime, while at atmospheric pressures CH$_4$ adsorption may saturate.

The practicality of lowering the adsorption temperature, however, is limited by cooling power of the system and the possibility of affecting other components. The two MOF candidates show a similar CH$_4$ adsorption behavior at 77 K (Fig. 9), but HKUST-1 has a much higher adsorption

| Table 1 Physical properties of the tested adsorbents for CH$_4$ |
|---------------------------------------------------------------|
| Density (g/cm$^3$) | BET surface (m$^2$/g) | Langmuir surface (m$^2$/g) | $\Delta H^0_{CH_4}$ (virial) (kJ/mol) | $\Delta H^0_{CH_4}$ (interpolation) (kJ/mol) |
| HayeSep D | 0.33$^a$ | 850–900 | (1200–1400) | 19.9 | 21.0 |
| MWCNT | 0.21$^b$ | 500 | (550) | 15.8 | 13.7 |
| HKUST-1 | 0.35$^a$ | 1500–2200 | (5000–+ | 15.7 | 15.1 |
| ZIF-8 | 0.35$^a$ | 1250–1750 | (2000) | 14.0 | 12.5–13.5 |
| Z5A | 0.72$^a$ | (552) | 622 | 21.2 | 21.0 |
| Z13X | 0.65$^a$ | (510) | 794 | 18.3 | 17.6 |

| Nitrogen |
|-----------------------------------------------|
| BET surface (m$^2$/g) | Langmuir surface (m$^2$/g) | $\Delta H^0_{N_2}$ (virial) (kJ/mol) | $\Delta H^0_{N_2}$ (interpolation) (kJ/mol) |
| HayeSep D | 600–700 | (640) | 12.6 | 13.7 |
| MWCNT | 350–400 | (350–400) | 14.1 | 16.9 |
| HKUST-1 | (1450–1550) | 1680 | 14.1 | 14.2 |
| ZIF-8 | (1450–1600) | 1700 | 11.4 | 12.3 |
| Z5A | (462) | 537 | 26.1 | 25.0 |
| Z13X | (540) | 628 | 18.3 | 18.9 |

| Selectivity |
|----------------|
| CH$_4$ adsorption$^c$ (mmol/g) | N$_2$ adsorption$^c$ (mmol/g) | Selectivity (X) (n$_{CH_4}$/n$_{N_2}$) | $\Delta H^0_{CH_4}$ (kJ/mol) | $\Delta H^0_{N_2}$ (kJ/mol) | Selectivity (Y) ($\Delta H^0_{CH_4}/\Delta H^0_{N_2}$) |
| HayeSep D | 1.78 | 0.49 | 3.7 | 19.9 | 12.6 | 1.6 |
| MWCNT | 1.45 | 0.51 | 2.9 | 15.8 | 14.1 | 1.1 |
| HKUST-1 | 10.71 | 3.80 | 2.8 | 15.7 | 14.1 | 1.1 |
| ZIF-8 | 4.02 | 0.77 | 5.2 | 14.0 | 11.4 | 1.2 |
| Z5A | 3.42 | 2.63 | 1.3 | 21.2 | 26.1 | 0.8 |
| Z13X | 3.14 | 2.10 | 1.5 | 18.3 | 18.3 | 1.0 |

Values in parentheses indicate limited agreement between the experimental data and the model

$^a$ Sigma Aldrich

$^b$ Cheap tubes Inc. Values in parentheses indicate limited agreement between the experimental data and the model

$^c$ Excess adsorption amount at 100 kPa at 196 K for CH$_4$ and N$_2$ respectively
capacity at 196 K (Fig. 10). This is attributed to the low isosteric enthalpy of adsorption of ZIF-8 for CH$_4$ (Table 1). Therefore, ZIF-8 may be a promising adsorbent for methane preconcentration when the necessary cooling conditions are available.

Practically, the desorption temperature can be as high as necessary. A temperature of $\approx$ 273 K should be sufficient to desorb 99.99% of the captured CH$_4$, as it has shown to be an ideal regime for the desorption of N$_2$O from HayeSep D (Mohn et al. 2010). The optimal desorption temperature is likely to follow with the isosteric enthalpy of adsorption for CH$_4$, so that for example ZIF-8 would retain even less CH$_4$ than HayeSep D at $\approx$273 K.

4.6 Co-adsorption

Methane adsorption from ambient air represents a big challenge as a very small volumetric mixing ratio around $2 \times 10^{-6}$ has to be separated from many other gases, such as N$_2$ (78%), oxygen (20.9%), argon (0.9%), water vapor (variable content), carbon dioxide ($400 \times 10^{-6}$) and nitrous oxide ($0.3 \times 10^{-6}$). The focus of the presented study was on the separation of CH$_4$ from N$_2$, which is by far the dominating component in ambient air. With respect to our target application it is not necessary to address possible co-adsorption differences between the materials with respect to oxygen (O$_2$), argon (Ar) and other noble gases, assuming that in a first approximation, the effects will be similar for the materials studied. Nonetheless, additional experiments on the separation of O$_2$ and Ar may be needed for other applications. Similarly, the adsorption of carbon dioxide (CO$_2$) and water vapor (H$_2$O) is of minor importance because both are routinely removed prior to CH$_4$ adsorption in the envisaged analytical applications (Mohn et al. 2010; Bock et al. 2010). Nitrous oxide (N$_2$O) has much lower ambient air mixing ratios and a higher boiling point than CH$_4$. Therefore, it is of lower importance and could be separated by selective desorption.

4.7 Limits of the approach

Additionally to the limits mentioned in Sects. 4.4 and 4.6 there are also other considerations to make for this approach. The proposed material selection methodology focuses entirely on adsorptive selectivity, but does not consider any other properties which may be relevant, such as dispersion coefficients or thermal conductivity (Wiersum et al. 2013; Saridara et al. 2010). The former is due to the kinetic behavior of gases inside the pores and is thus related to the pore-size distribution of the adsorbent. The kinetic behavior of gases inside the pores of zeolites is well known, and also investigated for MOFs (Yaremov et al. 2013; Li et al. 2009). Thermal conductivity is important in order to remove the large amount of heat being added to the system by the adsorbed gas. While these general material properties may be known, the behavior of a specific setup is difficult to predict. Therefore, these properties are best determined in breakthrough experiments which reflect the conditions that are expected for the target preconcentration setup. Our approach is based on the approximation of the selectivity of CH$_4$ over N$_2$. While this is a valuable first approximation, it may not reflect the full
complexity of the kinetic effects that are present during methane preconcentration of ambient air.

5 Conclusion

In this study we have systematically evaluated six adsorbent materials for the application of high volume preconcentration of ambient air, with the aim of categorizing each material in adsorption capacity and CH$_4$/N$_2$-selectivity. For effective high volume preconcentration, the overall adsorption capacity becomes a critical parameter in addition to CH$_4$/N$_2$-selectivity. Thus, HKUST-1 is highly promising due to its good selectivity and exceptional total adsorption capacity compared to HayeSep D. ZIF-8 also exhibits a high surface area, which is similar to HKUST-1, and even better selective properties. However, due to the weak binding interaction of ZIF-8 with CH$_4$, its adsorption capacity is lower compared to HayeSep D in the low pressure and high temperature regime. MWCNT exhibits a good selectivity, but the overall adsorption capacity is much lower than HayeSep D or HKUST-1. Carbon nanotubes with higher surface areas could therefore also be promising materials, especially because of their high thermal conductivity (Saridara et al. 2010; Han and Fina 2011). The zeolites have a low adsorption capacity and the lowest selectivity making them the least suitable candidates according to this study.

In conclusion, our data confirms that HayeSep D, a frequently used adsorbent for analytical preconcentration applications, is a suitable choice. It has a respectable adsorption capacity and the highest overall selectivity. The optimal adsorbent, however, would have a higher surface area combined with the isosteric enthalpy and selectivity of HayeSep D. We therefore suggest that a microporous equivalent of HayeSep D would be an ideal future material for this purpose. The approach used in this study is suitable for identifying candidate materials for high volume preconcentration of CH$_4$ from ambient air, and can easily be extended by additional gas compounds such as O$_2$, Ar and N$_2$O, as well as to other applications.

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