Mixed gas adsorption of carbon dioxide and methane on a series of isoreticular microporous metal–organic frameworks based on 2-substituted imidazolate-4-amide-5-imidates†

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In this work the adsorption of CO₂ and CH₄ on a series of isoreticular microporous metal–organic frameworks based on 2-substituted imidazolate-4-amide-5-imidates (IFP-1–IFP-6, IFP = Imidazolate Framework Potsdam), is studied firstly by pure gas adsorption at 273 K. All experimental isotherms can be nicely described by using the Tóth isotherm model and show the preferred adsorption of CO₂ over CH₄. At low pressures the Tóth isotherm equation exhibits a Henry region, wherefore Henry’s law constants for CO₂ and CH₄ uptake could be determined and ideal selectivity α_{CO₂/CH₄} has been calculated. Secondly, selectivities were calculated from mixture data by using nearly equimolar binary mixtures of both gases by a volumetric–chromatographic method to examine the IFPs. Results showed the reliability of the selectivity calculation. Values of α_{CO₂/CH₄} around 7.5 for IFP-5 indicate that this material shows much better selectivities than IFP-1, IFP-2, IFP-3, IFP-4 and IFP-6 with slightly lower selectivity α_{CO₂/CH₄} = 4–6. The preferred adsorption of CO₂ over CH₄ especially of IFP-5 and IFP-4 makes these materials suitable for gas separation application.

1 Introduction

Recently we synthesized a new series of isoreticular metal–organic frameworks, IFP-1, IFP-2 IFP-3, IFP-4, IFP-5 and IFP-6, based on 2-substituted imidazolate-4-amide-5-imidates (Scheme 1). The 2-substituted imidazolate-4-amide-5-imidates, 1a–1d (R = methyl), 1b (R = chloro), 1c (R = bromo), 1d (R = ethyl), link with the metal ions (IFP-1–IFP-4: Zn²⁺, IFP-5: Co²⁺, IFP-6: Cd²⁺) and form neutral microporous imidazolate metal–organic frameworks with 1D hexagonal channels. The chelate ligands 1a–1d show a strong structure-directing effect: the combination of amide/imidate and imidazolate groups causes a strong tendency for coordination and generates a permanent porosity in the IFPs. The rigidity and stability of 1a–1d also impart excellent thermal and water stability to the IFPs. Moreover, the imidazolate-amide-imidate linkers polarize the walls of the microporous channels. The 2-substituent R of the linkers 1a–1d protrudes into the open channels (Scheme 1). For this...
reason the accessible diameter and the functionality of the hexagonal channel in an IFP can be tuned by varying R. Furthermore the radius of the metal ion defines the channel diameter of an IFP. The accessible diameters of the channels in the IFPs are in the range of 1.7 to 5.2 Å (Scheme 1). In opposite to the tetrahedral coordination of the metal ions in well known ZIFs, the metal ion in an IFP is pentacoordinated by the imidazolate-amide-imidate linkers to form a distorted environment with a trigonal-bipyramidal character. That means the IFP surface bears exposed metal centers. These can dramatically enhance (selective) gas uptake or serve as a source of catalytic activity. The IFPs, IFP-1 to IFP-4, have significant capacity for the capture of CO₂ and a lower uptake capacity for CH₄. In general higher uptakes of CO₂ in comparison to CH₄ are justified as well as with the exposed Zn²⁺ centers provided by IFP-3, IFP-4, and IFP-5, the mixture adsorption equilibrium time was set to more than 70 hours for both. For IFP-1, IFP-2, IFP-3 and IFP-5 the equilibrium time was set to 24 hours.

Based on a mass balance that includes the knowledge of vessel volume, pressure, temperature and gas phase concentration, the adsorbed amount can be calculated. The surface excess can further be determined by choosing the sample volume from gravimetric measured He isotherms.

In addition, different pressure transducers (Newport Omega, USA) were used in a range from vacuum up to 5 MPa with an accuracy of 0.05%. The temperature was kept constant with an accuracy of ±0.1 K. The gas phase concentration was analyzed offline using a Chrompack GC CP9001 (separation column: CarboPlot (25 m × 0.53 mm)) and Ar as the carrier gas by a thermal conductivity detector. Therefore, the gas phase was transferred to a sampling system, so that 100 μL of the gas mixture can be taken by a gas-tight syringe and furthermore transferred to the GC.

For the determination of the density from pressure, temperature and gas phase concentration, a calculation tool was used, which includes the equation of state based on GERG.² A detailed procedure of binary adsorption measurement using this set-up as well as a schematic view of the system and a reference experiment using a well known activated carbon is given in ref. 8.

### 3 Theoretical section

Based on the simple Langmuir equation, a model is used, which can describe pure gas adsorption isotherms in a wide range of pressure. The Töth isotherm equation (eqn (1)) is a good description for this purpose and, as an advantage, this equation is a thermodynamically correct isotherm equation

\[ \frac{n}{n_\infty} = \frac{bp}{(1 + b)^{t/2}} \]  

(1)

\( n \) —adsorbed amount, \( n_\infty \) —maximum adsorbed amount, \( b \) —the Töth isotherm constant, and \( t \) —parameter related to the heterogeneity of the surface.¹¹²

At low pressures the Töth isotherm equation exhibits a Henry region, where one can estimate the Henry’s law constant, which is given by

\[ H = bn_\infty^t \]  

(2)

By applying a fitting procedure of each isotherm, the average relative deviation between the experimental and modeled isotherm point was used for each isotherm by

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\[
\Delta n^0 = \frac{100}{N} \sum_{i=1}^{N} \left( \frac{n_{\exp}^i - n_{\text{mod}}^i}{n_{\exp}^i} \right)
\]  
\tag{3}
\]

\(N\)—the number of isotherm points, \(n_{\exp}^i\)—experimental, and \(n_{\text{mod}}^i\)—modeled isotherm point).

The ideal adsorbed solution theory (IAST) was used for the prediction of multi-component adsorption equilibria.\(^{12,13}\) The theory is based on an ideal adsorbed phase, where no interaction between the adsorbed molecules takes place. Analogous to Raoult’s law, equilibria conditions can be described by

\[
y_i p = p_i^0 (y_i^0)^{x_i}
\]  
\tag{4}
\]

\(p\)—pressure, \(y_i\)—gas phase concentration of component \(i\), \(x_i\)—adsorbed phase concentration of component \(i\) and \(p_i^0\)—equilibrium pressure for pure component \(i\).

\(p_i^0\) corresponds to the reduced spreading pressure of the mixture. The reduced spreading pressure can be expressed as

\[
\frac{\pi A}{RT} = \frac{1}{n(0)} \ln(p_0)
\]  
\tag{5}
\]

and calculated by using the Töth isotherm model for pure gas adsorption isotherms. The spreading pressure can then be obtained for pure component \(i\) at a given \(y\) and \(p\). By assuming a constant spreading pressure for each component

\[
x_i^0 = x_j^0 = \ldots = x_n^0
\]  
\tag{6}
\]

the adsorbed phase concentration \(x_i\) can be calculated. Furthermore, the Lewis rule makes it possible to evaluate the adsorbed amount of all components

\[
\frac{1}{n^0} = \sum_i \frac{x_i}{n_i^0}
\]  
\tag{7}
\]

With the gas phase and adsorbed phase molar fraction from the binary adsorption measurements or from IAST prediction, the adsorption selectivity \(\alpha\) for the components \(i\) and \(j\) is given as:\(^{14}\)

\[
\alpha_{ij} = \frac{x_j}{y_j} \left/ \frac{x_i}{y_i} \right.
\]  
\tag{8}
\]

In contrast, a value for selectivity can also be given from the pure gas adsorption isotherm. As followed by thermodynamics, the adsorption selectivity from expression (8) can be rearranged by the formulation of the Henry law to be

\[
\lim_{p \to 0} \alpha_{ij} = \left( \frac{n_j}{y_j} \right) \left/ \left( \frac{n_i}{y_i} \right) \right. \right. = \frac{H_i}{H_j}
\]  
\tag{9}
\]

The selectivity derived by the Henry’s law constants is a limit case and is valid for zero coverage of the solid surface.

4 Results and discussion

4.1 Adsorbent characterization

As already discussed in a previous work,\(^2\) \(N_2\) adsorption is not the most appropriate method to characterize the textural properties of porous materials with narrow micropores. As in the case of IFP-1 to IFP-4 better results are observed by measuring \(CO_2\) adsorption at 273 K.\(^2\) Therefore, \(CO_2\) adsorption at 273 K was used to characterize the textural properties of all IFP materials in this study. By applying the BET method for microporous material\(^{15}\) to the \(CO_2\) adsorption isotherms (cross-sectional area of \(CO_2\) to be 0.21 nm\(^2\)), the calculated BET surface areas decrease in the range \(IFP-1 > IFP-6 > IFP-2 > IFP-4 > IFP-3 > IFP-5\) (Table 1). This ordering correlates especially in the case of \(IFP-6\) and \(IFP-4\) not with the range of decreasing effective channel diameters as shown in Scheme 1. We assume that activated \(IFP-6\) contains smaller channels (3–4 Å) than it was determined from an as-synthesized crystal by X-ray crystallography (5.2 Å).\(^3\) \(IFP-4\) contains flexible ethyl groups. The effective channel diameter of 1.7 Å for \(IFP-4\) (Scheme 1) is calculated\(^2\) and is only based on the conformation of the ethyl group at the energy minimum. Recently, Henke and Fischer showed that flexible methoxymethoxy groups in a honeycomb-like zinc–dicarboxylate–bipyridine framework act as molecular gates for guest molecules and allow highly selective sorption of \(CO_2\) over \(CH_4\).\(^{16}\) The ethyl groups in \(IFP-4\) also have the potential to function as molecular gates for guest molecules. \(CO_2\) can fill the whole pore volume of the porous material \(IFP-1\) to \(IFP-6\) at 273 K. By assuming that the adsorbate is in the liquid-like state at the saturation regime of the isotherms, one can apply the Gurvich rule (here at \(p/p_0 = 0.5\)) and the Dubinin–Radushkevich method for estimation of the pore volume.\(^{17}\) The calculated values of the BET surface area can then be slightly different from values given in ref. 2, because of the difference in applied methods.

4.2 Pure gas adsorption

In Fig. 1 and 2, all \(CO_2\) and \(CH_4\) adsorption isotherms on IFP materials \(IFP-1\) to \(IFP-6\) are shown. For \(CH_4\) no surface excess maximum was found until 5 MPa, whereas for \(CO_2\) in some cases a surface excess maximum could be indicated. This is due to the fact that the adsorbed phase of \(CO_2\) is at 273 K more compressible than the adsorbed phase of \(CH_4\).\(^{15,16}\) At higher pressures a maximum for \(CH_4\) can be observed, as shown in ref. 2. Hence for fitting the \(CO_2\) adsorption isotherm all points were used before the maximum in surface excess was reached. All isotherms were then well described by the Töth isotherm equation. An overview of fitting parameters is given in Table 2 and 3 including the average relative derivations. These values are quite

| Material | \(A_{\text{BET}}/\text{m}^2\ \text{g}^{-1}\) | \(V_{\text{Pore}}/\text{cm}^3/\text{cm}^{-3}\) | \(V_{\text{Pore}}/\text{cm}^3/\text{cm}^{-3}\)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>IFP-1</td>
<td>1068</td>
<td>0.31</td>
<td>0.32</td>
</tr>
<tr>
<td>IFP-2</td>
<td>940</td>
<td>0.26</td>
<td>0.28</td>
</tr>
<tr>
<td>IFP-3</td>
<td>622</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>IFP-4</td>
<td>674</td>
<td>0.22</td>
<td>0.23</td>
</tr>
<tr>
<td>IFP-5</td>
<td>574</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>IFP-6</td>
<td>985</td>
<td>0.27</td>
<td>0.28</td>
</tr>
</tbody>
</table>

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CO₂ consists of a quadrupole, whereas CH₄ is nonpolar. IFP adsorbs CO₂ stronger than CH₄ and therefore allows CO₂ adsorption at lower pressures than CH₄. In addition, IFP adsorbs CO₂ at high pressures by all IFPs, which is indicated by the Henry's law constants given in Table 2.

\[
\begin{array}{cccccc}
\text{Töth parameter} & n_{\text{eq}} & b & t & H/L & \Delta n^*(\%) \\
n\text{mmol g}^{-1} & \text{mmol g}^{-1} \text{MPa}^{-1} & \text{MPa}^{-1} & \text{mmol g}^{-1} \text{MPa}^{-1} & \% \\
\text{IFP-1} & 7.077 & 11.64 & 0.824 & 82.37 & 1.63 \\
\text{IFP-2} & 5.885 & 15.74 & 0.886 & 92.60 & 2.67 \\
\text{IFP-3} & 4.077 & 22.56 & 0.735 & 91.99 & 3.49 \\
\text{IFP-4} & 3.387 & 35.03 & 0.457 & 221.71 & 0.57 \\
\text{IFP-5} & 4.770 & 31.67 & 0.517 & 151.09 & 2.27 \\
\text{IFP-6} & 5.962 & 9.79 & 0.966 & 58.37 & 4.12 \\
\end{array}
\]

At higher pressures, the adsorbed amount of CO₂ is higher than that for CH₄, because CO₂ is below its bulk critical temperature \(T_{C,CO₂} = 304.15\) K, whereas CH₄ \(T_{C,CH₄} = 190.55\) K is supercritical.

### 4.3 Mixed gas adsorption

In order to assess the separation potential and to classify the isoreticular series of IFPs, binary adsorption of nearly equimolar mixture of CO₂ and CH₄ was measured at 273 K and 0.1 MPa for each IFP material by a volumetric–chromatographic method. Additionally, binary adsorption was predicted using the IAST in comparison with the pure gas adsorption Töth isotherm model for spreading pressure calculations. For all IFP materials the indicating spreading pressure diagram can be found in the ESI (Fig. S1–S6†). The partial molar loadings are given in Fig. 3a–f. In all cases the IAST + Töth isotherm model predicts well the mixture adsorbed amount, so that one can obtain an ideality of the adsorbed phase. The calculated relative derivations between experimental data and IAST prediction are given in Table 4, which differ slightly between IFP materials. For IFP-6 the derivations are higher than in the case of the other IFP materials affected by the very low kinetic to reach adsorption equilibria. In that case more than 60 hours equilibrium time was chosen for measurement of binary mixtures.

The ideality of the adsorbed phase can also be seen in Fig. 4 (McCabe–Thiele diagrams), where the adsorbed phase molar fraction \(x_{CO₂}\) is plotted against the gas phase molar fraction \(y_{CO₂}\). From such plots it is obvious that the adsorption of CO₂ is preferred over CH₄ adsorption for IFPs over the whole gas phase composition. If the IAST predicts the \(x-y\) distribution in a good manner, then the selectivity should be as well, which can be seen in Fig. 4, where the selectivities at 0.1 MPa and 273 K calculated from IAST are compared to experimental data.

It is obvious that for IFP-1, IFP-2, IFP-3 and IFP-6 the selectivities with \(\alpha_{CO₂/CH₄}\) around 4–5 are lower than for IFP-4 (around 6) and IFP-5 (around 7.5) (Fig. 5). As already mentioned IFP-4 consists of an open void space of 1.7 Å (without solvent or gas molecules in the void space) and ethyl groups from the ligand on the edge of these voids. Incoming gas molecules have to widen the void space by changing conformation of the ethyl groups arranged on the Cl-atom of the imidazole ring. Because of the lower kinetic diameter of CO₂ (3.3 Å) in comparison to CH₄ (3.8 Å), the twist of the ethyl groups for incoming CO₂ has to be smaller as it has to be for CH₄.
Fig. 3  (a–f) Partial molar loadings of CO$_2$ and CH$_4$ on (a) IFP-1, (b) IFP-2, (c) IFP-3, (d) IFP-4, (e) IFP-5, and (f) IFP-6.

Table 4  Binary adsorption of CO$_2$/CH$_4$ on IFP materials at 273 K and deviation between experimental data and prediction by IAST; adsorption selectivities for CO$_2$/CH$_4$ on IFP materials at 273 K

<table>
<thead>
<tr>
<th>Material</th>
<th>$p$/MPa</th>
<th>$y_{CO_2}$</th>
<th>$x_{CO_2}$</th>
<th>$\Delta x_{CO_2}$ (%)</th>
<th>Equilibrium time/h</th>
<th>$n'_{CO_2}$/mmol g$^{-1}$</th>
<th>$\Delta n'_{CO_2}$/mmol g$^{-1}$</th>
<th>Ideal selectivity from Henry’s law constants</th>
<th>Experimental selectivity $\alpha_{CO_2/CH_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IFP-1</td>
<td>0.1017</td>
<td>0.478</td>
<td>0.799</td>
<td>1.12</td>
<td>22</td>
<td>2.074</td>
<td>3.98</td>
<td>2.594</td>
<td>3.89</td>
</tr>
<tr>
<td></td>
<td>0.0991</td>
<td>0.496</td>
<td>0.807</td>
<td>0.51</td>
<td>46</td>
<td>2.065</td>
<td>2.14</td>
<td>2.558</td>
<td>1.64</td>
</tr>
<tr>
<td>IFP-2</td>
<td>0.0948</td>
<td>0.514</td>
<td>0.836</td>
<td>0.10</td>
<td>20</td>
<td>2.010</td>
<td>4.05</td>
<td>2.500</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td>0.0970</td>
<td>0.514</td>
<td>0.836</td>
<td>0.10</td>
<td>4</td>
<td>2.150</td>
<td>0.26</td>
<td>2.571</td>
<td>0.16</td>
</tr>
<tr>
<td>IFP-3</td>
<td>0.0989</td>
<td>0.492</td>
<td>0.826</td>
<td>0.08</td>
<td>20</td>
<td>1.455</td>
<td>1.65</td>
<td>1.762</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>0.1009</td>
<td>0.521</td>
<td>0.838</td>
<td>0.53</td>
<td>6</td>
<td>1.500</td>
<td>3.23</td>
<td>1.790</td>
<td>2.69</td>
</tr>
<tr>
<td>IFP-4</td>
<td>0.0969</td>
<td>0.490</td>
<td>0.853</td>
<td>1.49</td>
<td>22</td>
<td>1.651</td>
<td>3.20</td>
<td>1.935</td>
<td>1.73</td>
</tr>
<tr>
<td></td>
<td>0.1016</td>
<td>0.504</td>
<td>0.854</td>
<td>0.77</td>
<td>6</td>
<td>1.709</td>
<td>3.03</td>
<td>2.000</td>
<td>2.27</td>
</tr>
<tr>
<td>IFP-5</td>
<td>0.0999</td>
<td>0.502</td>
<td>0.883</td>
<td>0.58</td>
<td>19</td>
<td>1.494</td>
<td>3.50</td>
<td>1.692</td>
<td>2.94</td>
</tr>
<tr>
<td></td>
<td>0.1008</td>
<td>0.521</td>
<td>0.890</td>
<td>0.32</td>
<td>4</td>
<td>1.475</td>
<td>0.27</td>
<td>1.657</td>
<td>0.63</td>
</tr>
<tr>
<td>IFP-6</td>
<td>0.1050</td>
<td>0.560</td>
<td>0.860</td>
<td>0.59</td>
<td>65</td>
<td>1.873</td>
<td>5.63</td>
<td>2.179</td>
<td>5.01</td>
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<tr>
<td></td>
<td>0.1038</td>
<td>0.515</td>
<td>0.866</td>
<td>2.90</td>
<td>69</td>
<td>1.836</td>
<td>0.32</td>
<td>2.122</td>
<td>3.31</td>
</tr>
</tbody>
</table>
Therefore, IFP-4 shows higher selectivity compared to IFP-1 to IFP-3 and IFP-6. In contrast, IFP-5 has the highest selectivity in this series of IFPs with a CO2/CH4 around 7.5 at 273 K and 0.1 MPa. That might be due to the presence of the unsaturated metal site of the paramagnetic Co centre. We assume that the Co centres in IFP-5 have a higher potential to polarize CO2 molecules than the Zn and Cd centres in the other IFPs.

In Table 4, the selectivities obtained from experimental data are shown. Such values differ from ideal selectivity due to the Henry’s law region of pure gas isotherms (Table 2 and 3). However, the trend between all IFP materials is the same.

However, with the preferred adsorption of CO2 over CH4, this series of IFPs and especially IFP-5 could be a promising candidate for biogas purification or for CO2 capture from CH4-based gas mixtures on the equilibrium effect. In more detail, state-of-the-art adsorbents like activated carbons show slightly lower selectivities for CO2 within a range of a CO2/CH4 = 2–618,21 than in the case for IFP-5. Whereas hydrophilic zeolites show higher affinity towards H2O and CO2 resulting in a higher selectivity for the separation of CO2 from a CO2/CH4 mixture. Zeolites have at a slightly higher temperature regime (273 K < T > 333 K) selectivities of about a CO2/CH4 > 6,18,22–24 and in addition the disadvantage that the CO2 adsorption capacity depends on the value of preadsorbed H2O. Thus, the reactivation of such materials might be problematic. The selectivity of IFP-5 is just higher than for porous clays (a CO2/CH4 = 2–3).27 Comparing to MOFs, the equilibrium selectivities of IFP-4 and IFP-5 are in the same order of magnitude as in the case of HKUST-1 (a CO2/CH4 = 5–7 at 0.1 MPa and 303 K),28 MIL-53-Al (a CO2/CH4 = 7 below 0.5 MPa and 303 K),29 MIL-53-Cr (a CO2/CH4 = 3–15 at different pressures and 303 K)30 and MIL-101-Cr (a CO2/CH4 = 3.6–7.5 at different pressures and 298 K),31 but lower than for amine-functionalized MIL-101-Al (a CO2/CH4 = 30–50 at 298 K).31

Eventually, IFP-4 and IFP-6 could be also promising candidates for the exploitation of a kinetic separation. Regarding their small void space, both materials exhibit a molecular sieving effect, which will be studied further.

5 Conclusions

We carried out pure gas and binary gas adsorption measurements of CO2 and CH4 on an isoreticular series of IFP materials.
at 273 K. The experimental pure gas isotherms were well described by the Töth isotherm equation. Binary adsorption data were further predicted with IAST, which are in excellent agreement with experimental data.

From these data, we could show further that IFP materials can keep up with selectivities of other well known MOF materials (e.g. HKUST-1 and different MIL structures). The most promising CO$_2$/CH$_4$ gas selectivity in the series of IFP materials shows IFP-4 and IFP-5. The behaviour of IFP-5 could be explainable via enhancement of the electronic interaction between CO$_2$ and the unsaturated metal site of the paramagnetic Co centre. IFP-4 is the material with the smallest pore diameter when the pores are empty, they should be too small for incoming CO$_2$ or CH$_4$. But relatively mobile ethyl groups in 2-position of the linkers can widen the pores by incoming gas molecules at relatively high temperatures (here 273 K). Because of smaller CO$_2$ molecules in comparison to CH$_4$ incoming CO$_2$ has to widen the pores to a smaller extent. This effect in addition to the bigger interaction of CO$_2$ via its quadrupole and the free exposed zinc centre, the CO$_2$ uptake is strongly preferred over CH$_4$ uptake in this case.

Future studies will deal with the kinetic gas separation potential of IFP-4 and IFP-6, e.g. CH$_4$/N$_2$ or Ar/O$_2$ should be examined. Furthermore the influence of competing, polar water molecules on the capacity and selectivity of CO$_2$ in IFPs will be tested.

Acknowledgements

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Notes and references

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