H₂ and CH₄ Sorption on Cu-BTC Metal Organic Frameworks at Pressures up to 15 MPa and Temperatures between 273 and 318 K

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ABSTRACT

Sorption isotherms of methane and hydrogen on Cu₃(BTC)_2 have been measured in the temperature range from 273 to 318 K and at pressures up to 15 MPa. H₂ excess sorption capacities of the Cu₃(BTC)₂ amounted to 3.9 mg/g at 14 MPa. Promising maximum CH₄ excess sorption capacities on the same sample were reached at approximately 5 MPa. They amounted to 101, 100, 92 and 80 mg/g at 273, 278, 293 and 318 K, respectively. The sorbed phase density was essentially the same for all temperatures and amounted to ~600 kg/m³. Structural changes of the Cu₃(BTC)₂ samples after thermal activation and treatment with high pressure H₂ and CH₄ were tested. It was found that the initial micropore structure has virtually disappeared as evidenced by a decrease of the Langmuir specific surface area by a factor ~3 and CO₂ micropore volume by a factor of ~4 for H₂ and ~3 for CH₄. This is in line with an increase in the average pore diameter from initially 9.2 to 15.7 for H₂ and 12.8 for CH₄.

Keywords: Metal Organic Framework (MOF), Sorption, Methane, Hydrogen, Pore Structure

1. Introduction

The concept of reticular design in the synthesis of metal organic frameworks (MOF) permits custom-tailoring of regular pore structures on the nanometer scale [1]. This approach opens new perspectives for the development of gas and energy storage systems [2]. So far, the gas sorption capacity of metal-organic frameworks (MOF) of various chemical and structural compositions has mainly been determined at low pressures (< 0.1 MPa) and temperatures (77 to 87 K). Only a few studies [3,4] reported H₂ and CO₂ measurements at ambient temperatures (ideal operating temperature).

Several authors reported the internal structure of different MOFs [5,6]; however, significant amounts of side products were detected using the synthesis described by Chui et al. (1999)[5]. One major problem concerning the storage of gases on these materials at high pressures (> 1 MPa) and temperatures (especially at the activation temperature of 458 K) is their structural instability and hence, a decrease in specific surface area associated with structural rearrangements for Cu-(BTC) [6].

In this study the sorption capacities of CH₄ and H₂ on Cu₃(BTC)₂ (Copper benzene-1,3,5-tricarboxylate,C₁₈H₆Cu₃O₁₂) have been investigated at temperatures between 273 and 318 K and pressures up to 15 MPa. Specific surface areas (SSA) and pore size distributions (PSD) have been determined on untreated samples before and after high-pressure sorption experiments in order to detect any structural changes of the sample due to the interaction with the gases. A similar approach has been used by [7], who reported changes in SSA and PSD on MOF-5 during hydrogen sorption.

Two slightly different MOFs both consist of the same organic ligands but with different basic metals (Al³⁺ and Cr³⁺) [8]. At 77K the Al³⁺–MOF shows higher sorption capacities than the corresponding Cr³⁺ sample. However, both samples nearly show the same specific surface area of ~1000 m²/g (Figure 1). This finding confirms the importance of micropore volume and the electrostatical potential of the different metals.

Data provided in Figure 1 reflects the general correlation between SSA (determined by low pressure N₂-isotherms at 77 K) and H₂ sorption capacity at 77 K. It is known that this trend is ambiguous for isotherms recorded at higher temperatures [9]. One suggestion is that
a better correlation can be obtained by separating the hydrogen adsorbed in the micropores from that on the surface of the mesopores. Furthermore, Nijikamp et al. (2001) concluded that a higher storage capacity could be achieved with adsorbents containing a large micropore volume with suitable diameter [9].

In a study on hydrogen storage in chemically activated carbons and carbon nanomaterials, Beneyto (2007) [10] proposes that at 77 K the H2 adsorption capacity depends on the SSA and the total micropore volume of the activated carbon. At 298 K it depends on both the micropore volume and the micropore size distribution. To date, very few high pressure/temperature isotherms and corresponding micropore volumes have been determined on MOFs.

In comparison to hydrogen, it was shown for methane in different studies that Cu3(BTC)2 has a high CH4 storage capacity at room temperature [11,12] (295 to 298 K, Wang et al. 2002; Lin et al. 2006). Sorption values on Cu-BTC for CH4 of up to 72 mg/g (at 295 K and 0.1 MPa) with nearly linear sorption isotherms up to 0.1 MPa [11]. Maximum CH4 sorption capacities of 31.4 mg/g at 0.9 MPa and 298 K on Zn-MOF and a hysteresis between the sorption and desorption curves [12]. Senkovska and Kaskel (2007) [13] reported high pressure CH4 adsorption on Cu3(BTC)2, Zn2(bdc)2(dabco), Cr3F(H2O)2(O(bdc)), Among the three materials, Cu3(BTC)2 shows the highest excess adsorption at 303 K (15.7 mg/g).

2. Experimental

2.1. High-Pressure Sorption Experiments

High pressure single-gas adsorption experiments have been performed using a manometric experimental set-up (Figure 2) consisting of a stainless-steel measuring cell (MC) and a calibrated reference volume (RC) connected with a set of actuator-driven valves and a high-precision pressure transducer (max. pressure 25 MPa, with a precision of 0.05% of the full scale value). The entire device is placed in a temperature-controlled oven (variations in temperature < 0.1 K). Calculation of the excess sorption was performed based on equations of state by Setzman and Wagner (1991) [14] and McCarty et al. (1981) [15] for methane and hydrogen, respectively. Quality control is ensured by participation in laboratory comparison studies (e.g. Gensterblum et al. 2009 [16], 2010 [17] and Goodman et al. 2004 [18]). For further details on the experimental approach, please refer to e.g. Busch et al. (2004) [19].

As pointed out by Férey (2003) [8] for the MIL-53 and Schlichte et al. (2004) [6] for the MOFs - which were also investigated in this study - the activation of the metal-organic framework compounds is an important issue affecting the quality and reproducibility of sorption capacity measurements. The activation procedure was carried out in three stages: 12 h at 105°C, 12 h at 155°C, and finally 18 h at 185°C. This activation procedure led to well-reproducible starting conditions for the isotherm measurements.

Error bars shown in the diagrams and error margins listed in the Table 2 were determined based on the Gauss error propagation method considering the individual errors of the individual experimental parameters.

2.2. Characterisation of Pore Structure and Surface Area

A Quantachrome Autosorb 1 instrument was used to characterise the pore structure and surface properties of the samples. The latter has been performed using the equation proposed by Brunauer, Emmet and Teller (1938, BET) [20]. The pore size distribution for 1.2 up to 40 nm pore diameters were derived by NLDFT methods measured at 77 K. Pore size distributions (PSD) were analysed [21,22] and the nonlinear density functional theory (NL-DFT, Thommes et al. 2006) [23]. The submicromo- and micropores, in the range of 0.3 to 1.5 nm, were charac- terised by CO2 isotherms measured at 273 K. These iso- thermers were also evaluated according to the Dubinin and NL-DFT methods. For the NL-DFT evaluation, slit and/or cylindrical pores were assumed which
represents a compromise between availability of mathematical PSD-algorithms with spherical pore structure and real pore structures.

3. Results and Discussion

3.1. Sorption Capacities

3.1.1. Hydrogen

Figure 3 shows the H₂ excess sorption isotherms for Cu₃(BTC)₂ (HKUST-1), measured at 318 K, in comparison with similar literature data reported for Cu₃(BTC)₂ at 298 K [7]. The higher sorption capacities reported by Panella et al. (2005) [7] can be explained by lower experimental temperatures used. The rather linear trend (Freundlich or Langmuir-Freundlich type) of the sorption isotherms is comparable to other isotherm data (see Figure 1), but it is not a classical Langmuir type as would be expected for porous materials.

Structural changes (pore structure, specific surface area) of the Cu₃(BTC)₂ after H₂ sorption have been determined; the results are provided in Table 1. It is obvious that specific surface areas (SSA) decrease by a factor of 3-4, N₂ pore volumes by a factor of 2-3, and CO₂ micropore volumes by a factor of 4-5, while an increase in the Dubinin-Astakhov (DA) average pore diameter from 9.2 to 15.7 Å (10⁻¹⁰ m) can be observed.

Compared to the N₂ micropore volumes for Cu₃(BTC)₂ determined in this study 0.63 cm³/g (Table 1), several authors obtained values between 0.41 and 0.76 cm³/g on virgin samples [13,24,25]. Other studies report BET surface areas for this material of 1781 m²/g (single-point BET) [26], 1154 m²/g [7] and 1239 m²/g [11] which is similar to the BET surface area of 1246 m²/g ascertained in this study (all measured with N₂ at 77 K).

3.1.2. Methane

Methane sorption isotherms on Cu₃(BTC)₂ have been measured at temperatures between 273 and 318 K and pressures up to 15 MPa and are provided in Figure 4. Maximum excess sorption values obtained in these measurements are listed in Table 2. They show a generally decreasing trend with temperature from 101 to 79 mg CH₄/g MOF. After passing a maximum value, the excess sorption isotherms in Figure 4 decrease slightly until the final pressure value is reached. This decline above ~6 MPa can be attributed to a volumetric effect (non-negligible volume of the sorbed phase) that needs to be considered when calculating absolute sorption capacities. Among others, Humayun and Tomasko (2000) [27] proposed a method to determine the sorbed phase density, which has been applied in this study. This procedure resulted in nearly identical values of 597 to 601 kg/m³ for

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Table 1. Structural changes of Cu₃(BTC)₂ after high-pressure H₂ sorption experiment at 318 K. DR = Dubinin Radushkewic; NLDFT = non-local density functional theory.

<table>
<thead>
<tr>
<th>Cu₃(BTC)₂</th>
<th>method</th>
<th>N₂ surface area (m²/g)</th>
<th>CO₂ micropore surface area (m²/g)</th>
<th>N₂ pore volume (cm³/g)</th>
<th>CO₂ micropore volume (cm³/g)</th>
<th>DA pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>before H₂ sorption test</td>
<td>DR</td>
<td>1731</td>
<td>2708</td>
<td>0.63</td>
<td>0.94</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>NLDFT</td>
<td>1994</td>
<td>2340</td>
<td>0.64</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>after H₂ sorption test</td>
<td>DR</td>
<td>651</td>
<td>752</td>
<td>0.23</td>
<td>0.26</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>NLDFT</td>
<td>576</td>
<td>641</td>
<td>0.33</td>
<td>0.20</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. CH₄ Sorption parameters of Cu₃(BTC)₂ at 273 to 318 K considering helium densities.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>max. excess CH₄ sorption capacity (mg/g)</th>
<th>absolute CH₄ sorption capacity (mg/g)</th>
<th>CH₄ sorbed phase density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>101 ± 7</td>
<td>113 ± 3</td>
<td>599 ± 10</td>
</tr>
<tr>
<td>278</td>
<td>100 ± 7</td>
<td>112 ± 3</td>
<td>601 ± 8</td>
</tr>
<tr>
<td>293</td>
<td>92 ± 2</td>
<td>103 ± 2</td>
<td>597 ± 5</td>
</tr>
<tr>
<td>318</td>
<td>79 ± 2</td>
<td>90 ± 3</td>
<td>n.d.</td>
</tr>
</tbody>
</table>
H₂ and CH₄ Sorption on Cu-BTC Metal Organic Frameworks at Pressures up to 15 MPa and Temperatures between 273 and 318 K

the CH₄ sorbed phase density at three of the four experimental temperatures (Figure 5, Table 2). For the isotherm measured at 318 K, the pressure is not high enough for a graphical determination. This suggests that the density of the sorbed CH₄ phase is independent of the experimental temperature. Maximum absolute sorption capacities, taking into consideration the volume of the sorbed phase, have been determined to be as high as 113, 112, 103 and 90 mg/g at 273, 278, 293 and 318 K, respectively (Table 2), by applying the following relationship:

\[ n_{\text{abs}} = \left( \frac{1 + a p}{a p} \right) \left( \frac{n_{\text{ex}}}{\rho_{\text{gas}}} \right) \left( \frac{1}{\rho_{\text{sorbed}}} \right) \]  

(1)

where \( n_{\text{ex}} \) denotes the excess sorption capacity, \( \rho_{\text{gas}} \) the gas phase density, “a” is the Langmuir parameter (1/MPa) and \( \rho_{\text{sorbed}} \) the sorbed phase density as determined graphically in Figure 5.

The Langmuir curves shown in Figure 4 were calculated with explicit consideration of the sorbed phase density and therefore, reproduce the decline of the isotherms at high pressures.

In comparison to the study by Senkovska and Kaskel (2007) [13], the CH₄ sorption values in this study are lower by a factor of ~1.4. One explanation might be the reference to the sample mass (or sample density). Senkovska and Kaskel (2007) [13] used a crystallographic density of 0.88 g/cm³. In this study, sorption values are related to initial weight, while the sample density after activation is 1.77 ± 0.03 g/cm³ as determined by helium pycnometry. This lead to a slightly lower sorption amounts for this study in comparison to Senkovska and Kaskel (2007) [13].

3.2. Isosteric Heats of Adsorption

Based on the sorption isotherms measured between 273 and 318 K, isosteric heats of adsorption for CH₄ have been calculated using the Clausius-Clapeyron relation (Equation (2)). In this first approximation, the dependence of the adsorption enthalpy on surface coverage was neglected.

\[ \Delta h_{\text{ads}} = R \cdot \frac{T_2}{T_2 - T_1} \ln \left( \frac{p_2}{p_1} \right) = R \cdot \frac{T_2}{T_2 - T_1} \ln \left( \frac{a_1}{a_2} \right) \]  

(2)

where \( T_1 \) and \( T_2 \) are 273 and 318 K, respectively, \( p_1 \) and \( p_2 \) are the CH₄ pressures for each isotherm corresponding to an equal fractional coverage \( \Theta \) and \( R \) denotes the universal gas constant. The parameters \( a_1 \) and \( a_2 \) are constants derived from the linearised Langmuir curve for the two temperatures. For further details, please refer to Panella et al. (2006) [3].

The isosteric heat of adsorption was calculated based on a Langmuir fit of the experimental data. The decrease in CH₄ excess sorption at pressures above 10 MPa is reproduced by introducing a term that accounts for the increase in sorbed phase volume with increasing loading (Equation (1)). For this purpose, the density of the sorbed phase was determined graphically (see Figure 5). The procedure resulted in a very good fit (Figure 4) of the experimentally determined excess sorption values. The Langmuir parameters \( a_1 \) and \( a_2 \) obtained with this method for isotherms at two different temperatures were used in Equation (2) for the calculation of the isosteric heat of adsorption.

Isosteric heats of adsorption for CH₄ show an average value of ~11.2 ± 0.7 kJ/mol. In this case, a constant density of the sorbate phase was assumed. Using the parameters for the best least square Langmuir fit, an average value of ~12.2 ± 0.7 kJ/mol was obtained. Evaluation of the isosteric heat of adsorption in the low pressure
range (0 - 4 MPa) with the linearised Langmuir fit (providing the same values of absolute adsorption as the graphical evaluation) results in a significantly higher value for the heat of adsorption \((-17.9 \pm 1.3 \text{ kJ/mol})\).

3.3. Impact of CH₄ Sorption on Pore-Size Distribution

The pore-size distributions of the initial Cu₃(BTC)₂ and the samples after successive CH₄ and H₂ sorption measurements were determined by N₂ adsorption at 77 K. In order to describe adsorption on a wider range of microporous materials the Dubinin-Astakhov (DA) equation was used (Dubinin and Astakhov, 1971) [21]. It is a generalized form of the Dubinin-Radushkevich (DR; Dubinin, 1975 [22]) equation and was found to reasonably fit adsorption data for heterogeneous micropores. The results of the evaluations according to the DA method are displayed in Figure 6; the pertaining fitting parameters are listed in Table 3. The heterogeneity value \(n\) is higher for homogeneous distributions and is typically between 1 and 3. For instance, zeolite has an \(n\)-value higher than 3, demonstrating that these materials are very homogeneous. In this study, a value of \(n = 1\) was determined for Cu₃(BTC)₂. The characteristic energy \(E\) after Dubinin (1975) was determined to be 20.97 kJ/mol for the initial (unspoiled) sample and ranged between 8 and 18 kJ/mol after high-pressure CH₄ and H₂ sorption tests. The interaction constant is given as \(k = 2.96 \text{ kJ nm}^3/\text{mol}\) for nitrogen.

From Figure 6 it is evident that CH₄ affects the stability of the MOF to a lesser extent than H₂. Although a significant decrease in total pore volume is shown after two successive CH₄ sorption experiments, accompanied by a shift to larger mean pore radii (4.7 Å for the original sample; 6.4 Å after six CH₄ sorption isotherms; Table 3), a reduction comparable to the H₂ treatment is only observed after 6 CH₄ sorption isotherms. As observed for the H₂ treatment, the pore volume in the 5 to 15 Å range is most heavily affected. In this study it is likely that we had chosen a slightly too high activation temperature. However the reason for the different influence of CH₄ and H₂ on the sample structure is not clear will be investigated in further detail in a follow-up study.

Results of the evaluation of the micropore structure of the Cu₃(BTC)₂ before and after high-pressure CH₄ sorption isotherms based on the DR method and the nonlinear density functional theory (NLDFT) are summarised in Table 4. These results also support a significant decrease in micropore volume and subsequent reduction in specific surface area of the sample after high-pressure CH₄ sorption tests.

Figure 7 compares the high-pressure CH₄ excess sorption isotherms measured on the initial Cu-BTC MOF with a decomposed sample of the same material at 293 K. The treated sample shows significantly lower sorption values (decrease of up to 40 mg/g) compared to the initial samples, while the shape of the isotherms is similar between the two isotherms.

4. Conclusions

At pressures up to 7 MPa, Cu-BTC MOF is one of the most promising MOF materials for methane storage with a large uptake capacity and an excess sorption of 9.2 wt% at 293 K. The repeated thermal activation and high-pressure sorption tests with CH₄ on HKUST-1 at temperatures between 273 and 318 K resulted in a reduction of specific micropore volumes and surface area. The processes behind the reduction of the specific micropore volumes and surface area during each CH₄ sorption test (Table 4) are ambiguous and further research on this topic is needed.

Recent studies indicate thermal deterioration effects and
**Table 3. Fitting parameters of the DA equation for micropore characterisation of Cu\(_3\)(BTC)\(_2\) before and after CH\(_4\) and H\(_2\) high-pressure sorption isotherms.**

<table>
<thead>
<tr>
<th></th>
<th>N(_2) characteristic energy (E) [kJ/mol]</th>
<th>DA heterogeneous value (n)</th>
<th>average pore radius [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial sample</td>
<td>20.97</td>
<td>1</td>
<td>4.7</td>
</tr>
<tr>
<td>after 2 CH(_4) isotherms</td>
<td>18.66</td>
<td>1</td>
<td>4.9</td>
</tr>
<tr>
<td>after H(_2) isotherms</td>
<td>11.17</td>
<td>1</td>
<td>5.8</td>
</tr>
<tr>
<td>after 6 CH(_4) isotherms</td>
<td>8.66</td>
<td>1</td>
<td>6.4</td>
</tr>
</tbody>
</table>

**Table 4. Results of pore structure analysis of Cu\(_3\)(BTC)\(_2\) before and after high-pressure sorption isotherms with CH\(_4\).**

<table>
<thead>
<tr>
<th>method</th>
<th>N(_2) surface area (m(^2)/g)</th>
<th>N(_2) pore volume (cm(^3)/g)</th>
<th>CO(_2) surface area (m(^2)/g)</th>
<th>CO(_2) micropore volume (cm(^3)/g)</th>
<th>N(_2) DA pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial sample</td>
<td>1731</td>
<td>0.62</td>
<td>2708</td>
<td>0.94</td>
<td>9.2</td>
</tr>
<tr>
<td>DR</td>
<td>1994</td>
<td>0.64</td>
<td>2340</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>NLDFT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>after 2 CH(_4) isotherms</td>
<td>1174</td>
<td>0.42</td>
<td>1226</td>
<td>0.43</td>
<td>12.4</td>
</tr>
<tr>
<td>DR</td>
<td>1186</td>
<td>0.55</td>
<td>1069</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>NLDFT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>after 6 CH(_4) isotherms</td>
<td>737</td>
<td>0.26</td>
<td>997</td>
<td>0.35</td>
<td>12.8</td>
</tr>
<tr>
<td>DR</td>
<td>591</td>
<td>0.48</td>
<td>887</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>NLDFT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

by interaction with atmospheric air could cause the observed degradation of the sample. Table 4 shows a stepwise deterioration of the sample after successive CH\(_4\) sorption isotherms and the thermal activation process on the identical sample. Further changes caused by exposure to the atmosphere (e.g. oxidation of the sample) can be neglected, since samples did not come in contact with atmospheric air from the beginning of the thermal activation process (only H\(_2\), CH\(_4\) and He). However, it is unclear as of yet why micropores volumes decrease drastically and larger pores remain preserved.

Finally, this study has shown that the CH\(_4\) sorbed phase density is, within reasonable errors, independent of temperature.

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**REFERENCES**


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