Supporting information

Control of interpenetration via \textit{in-situ} Lithium incorporation in MOFs and their properties in gas adsorptions and selectivities

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S-1. Experimental synthesis, characterization and measurements

Synthesis: Non-interpenetrated MOF-5

Non-interpenetrated MOF-5 was synthesized according the procedure reported by Bi Chen et al.\(^\text{[1]}\) A mixture of Zn(NO\(_3\))\(_2\)·4H\(_2\)O (0.314g, 1.2mmol) and terephthalic acid (0.0665g, 0.4mmol) were solved in 10 ml of N,N-Diethylformamide (DEF). The solution was transferred to an autoclave (35ml) and heated at 105 °C for 24h applying a temperature program of 1°C/min for heating and cooling rate. The obtained yellow solid was washed with DEF and immerse in dichloromethane for 1 day followed by drying at 150°C for 12 h under vacuum. The product was directly characterized using techniques such as XRD, BET, Gas adsorption etc. or kept in a glove box in case of long time storage. All the procedures were carefully handled under inert atmosphere (Ar) to avoid water and moisture.

Synthesis: Interpenetrated MOF-5

The interpenetrated MOF-5 was synthesized according the procedure reported by Bi Chen et al.\(^\text{[1]}\). The pre-dried solvent (N,N-Dimethylformamide, DMF) was obtained after addition of activated molecular sieves (4Å) and drying for 3 days. The Zn(NO\(_3\))\(_2\)·6H\(_2\)O (0.4399 g, 1.4789 mmol) was solved in pre-dried DMF (10 ml) to which a small volume of water (180 μl) was added followed by terephthalic acid (0.1843 g, 112 mmol). The clear mixture was transferred in a Teflon-liner autoclave (35 ml), closed and placed in an oven. The autoclave was heated at 120 °C for 24 h applying a heating and cooling rate of 1°C/min. The colorless cube like solid was washed with pre-dried DMF and dried at 150 °C under vacuum oven for 12h. The white solid product was stored in a glove box to avoid contact with water and moisture.

Synthesis: Lithium terephthalate (Li-BDC)

The synthesis of lithium terephthalate (Li-BDC) was done according the procedure described by Kaduk. Li\(_2\)O (0.3093 g, 0.01 mol) was dissolve in distillated water (40 ml). To this solution was added 1.6712 g (0.01 mol) of commercial terephthalic acid. The resulting solution was filtered and ethanol (40 ml) was added. A white solid was obtained after evaporating of the solvent over two days.

Characterization and measurement

Activation of the materials was done by evacuation under vacuum at 150°C overnight obtaining porous materials ready for the characterizations. The powder X-ray diffraction spectra (XRD) were collected using a BRUKER instrument applying a monochromatic Cu K\(^\text{α}\) radiation at ambient conditions. The FT-IR measurements were performed on a BRUKER instrument type VERTEX using powder samples. Thermogravimetric analyses (TGA-DSC) were carried out using a Netzsch (STA449c/3/G) instrument. Thermal analysis were performed using a heating rate of 5°C·min\(^{-1}\) under inert atmosphere (N\(_2\)-flow). The low-pressure gas adsorption isotherms were measured by the volumetric method on a Micromeritics instrument (ASAP2020). In all gas adsorption measurements 60-100 mg of sample was used. For the CO\(_2\), CH\(_4\) and N\(_2\) gas adsorption analyses gases of purity > 99.999% were applied. Prior to the adsorption measurements, the samples were evacuated at 200°C under
vacuum (initial activation) for about 3 h. The micro pore surfaces were calculated by the Brunauer-Emmett-Teller (BET) and Langmuir method. The linearized BET and Langmuir equation were fit to the data within the range 0.02 \( P/P_0 < 0.2 \) and \( P/P_0 > 0.99 \) were used for pore volume.

Table S1. The MOF-5 synthesizing condition and characteristic their properties

<table>
<thead>
<tr>
<th>MOFs</th>
<th>Zine source (g)</th>
<th>Ligand BDC (g)</th>
<th>Solvents (ml)</th>
<th>Reaction Temperature &amp;Time</th>
<th>Specific surface area (m(^2)·g(^{-1}))</th>
<th>Pore Volume (cm(^3)·g(^{-1}))</th>
<th>Gas adsorption (mmol·g(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zn(NO(_3))(_2)·4H(_2)O (0.314)</td>
<td>0.0665</td>
<td>DEF (10ml)</td>
<td>105°C, 24h</td>
<td>2913</td>
<td>3107</td>
<td>1.622</td>
<td>3.38</td>
</tr>
<tr>
<td>1</td>
<td>Zn(NO(_3))(_2)·4H(_2)O (3.14)</td>
<td>0.665</td>
<td>DEF (100ml)</td>
<td>105°C, 24h</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>2</td>
<td>Zn(NO(_3))(_2)·6H(_2)O (0.4399)</td>
<td>0.1843</td>
<td>DMF+H(_2)O (10ml+180μl)</td>
<td>120°C, 48h</td>
<td>792</td>
<td>788</td>
<td>0.308</td>
<td>4.65</td>
</tr>
<tr>
<td>2</td>
<td>Zn(NO(_3))(_2)·4H(_2)O (0.4399)</td>
<td>0.1843</td>
<td>DMF+H(_2)O (10ml+140μl)</td>
<td>120°C, 48h</td>
<td>724</td>
<td>954</td>
<td>0.40</td>
<td>N.A.</td>
</tr>
</tbody>
</table>


S-2. Powder X-ray diffraction (PXRD) analyses

![Fig. S1 The XRD pattern comparable of non-interpenetrated MOF-5, interpenetrated MOF-5 and simulation MOF-5](image-url)
Fig. S2 The XRD pattern comparable of xLi-Zn-PDC series

S-3. Thermal analysis of MOF-5 with and without lithium

Fig. S3 A comparison of thermal stability of pure MOF-5 and 3Li-MOF-5 via thermal gravity analysis (TG)
Fig. S5 The FT-IR spectra of Li-BDC comparable with BDC (Terephthalic acid)

Fig. S6. FT-IR spectra comparable of BDC, Li-BDC and 3Li-MOF-5
S-5. Gas adsorption analyses

Fig. S7 The isotherm of N\textsubscript{2} adsorption at 77K on non-interpenetrated MOF-5 and pore volume with pore width plot (inset figure).

Fig. S8 The isotherm of N\textsubscript{2} adsorption at 77K on interpenetrated MOF-5 and pore volume with pore width plot (inset figure).
Fig. S9 The isotherm of N\textsubscript{2} adsorption at 77K on xLi-Zn-PDC series MOFs

Fig. S10 The CO\textsubscript{2} and CH\textsubscript{4} adsorption capacity at 273K on non-interpenetrated MOF-5
Fig. S11 The CO$_2$ adsorption capacity at 273K (a) and 308K (b) and CH$_4$ adsorption capacity at 273K (c) on xLi-MOF-5 series.

Fig. S12 The CO$_2$ (a) and CH$_4$ (b) adsorption capacity at 273K and pressure up to 1 bar.
Table S2 Summary of surface, porosity and gas adsorption properties on MOF of Zn-PDC

<table>
<thead>
<tr>
<th>MOFs</th>
<th>BET (m²/g)</th>
<th>Langmuir (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore wide (nm)</th>
<th>CO₂⁺ (cm³/g)</th>
<th>CH₄⁺ (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oli-ZnPDC</td>
<td>172</td>
<td>175</td>
<td>0.0659</td>
<td>0.8201</td>
<td>1.5</td>
<td>0.91</td>
</tr>
<tr>
<td>3Li-ZnPDC</td>
<td>243</td>
<td>246</td>
<td>0.0936</td>
<td>0.8222</td>
<td>1.81</td>
<td>0.81</td>
</tr>
<tr>
<td>5Li-ZnPDC</td>
<td>274</td>
<td>275</td>
<td>0.1045</td>
<td>0.8201</td>
<td>1.91</td>
<td>1.06</td>
</tr>
<tr>
<td>10Li-ZnPDC</td>
<td>274</td>
<td>272</td>
<td>0.1058</td>
<td>0.8587</td>
<td>1.74</td>
<td>0.74</td>
</tr>
</tbody>
</table>

* The adsorption at 273K and pressure up to 1 atm.

S-6. Selectivity calculations using the Ideal Adsorbed Solution Theory (IAST) [2]

IAST (Ideal Adsorption Solution Theory) was used to predict binary mixture adsorption from the experimental pure-gas isotherms. In order to perform the integrations required by IAST, the single-component isotherms should be fitted by a proper model. In practice, several methods are available and for this set of data the Langmuir equation (eq. 1) was successful in fitting our data. As can be seen in Table S1, the model fits the isotherms very well.

\[
q = \frac{q_m b p}{1 + b p}
\]

(Eq.1)

Wherein, \( p \) is the pressure of the bulk gas at equilibrium with the adsorbed phase (bar), \( q \) is the adsorbed amount per mass of adsorbent (mmol/g), \( q_m \) is the saturation capacity (mmol/g), \( b \) is the affinity coefficient of adsorption sites (1/bar). The fitted parameters were then used to predict multi-component adsorption with IAST.

The selectivity \( S_{A/B} \) in a binary mixture of components A and B is defined as:

\[
S_{A/B} = \frac{x_A / y_A}{x_B / y_B}
\]

(Eq. 2)

Wherein, \( x_i \) and \( y_i \) are the mol fractions of component \( i \) (\( i = A, B \)) in the adsorbed and bulk phases, respectively.

Table S3: Langmuir parameter calculated CO₂/CH₄ selectivity in xLi-MOF-5 series.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Adsorbates</th>
<th>( q_m )</th>
<th>( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Li-MOF-5</td>
<td>CO₂</td>
<td>9.32</td>
<td>1.234E-03</td>
</tr>
<tr>
<td>1Li-MOF-5</td>
<td>CO₂</td>
<td>8.09</td>
<td>1.288E-03</td>
</tr>
</tbody>
</table>

To extract the coverage-dependent isosteric heat of adsorption, the data were modeled with a virial-type expression (eq. 1) composed of parameters $a_i$ and $b_i$ that are independent of temperature:

\[
\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i
\]

(Eq. 1)

Wherein, $P$ is pressure (mmHg), $N$ is the amount adsorbed (mmol/g), $T$ is temperature (K), and $m$ and $n$ determine the number of terms required to adequately describe the isotherm. Successive terms were included in the fitting expression until they did not appreciably reduce the $\chi^2$ goodness-of-fit; in all cases $m=4$ and $n=3$. From these results, the isosteric heat of adsorption is calculated according to eq. 2:

\[
Q_{st} = -R \sum_{i=0}^{m} a_i N^i
\]

(Eq. 2)

Wherein, $R$ is the universal gas constant. The coverage dependencies of $Q_{st}$ calculated from fitting the 0 and 25°C data are presented graphically in figure below, as well as the goodness of fit.

The isosteric heats of adsorption curves are compared. Determining the correct isosteric heats of adsorption is particularly important for applications in CO$_2$ storage in order to design materials that have optimal CO$_2$ binding enthalpies over the entire loading range of interest. The observed difference in trends can be attributed primarily to differences in the agreement between the experimental and calculated isotherms. While small differences in the quality of the isotherm fits may not seem to be important, they can have dramatic effects on the shape of the isosteric heat of adsorption curves, especially at lower loadings. Based on visual inspection and comparison of statistical parameters, the Virial methods described above seem to give very good descriptions of the experimental isotherms. However, when the isotherms and corresponding fits are plotted on a log-scale, significant differences in the quality of the fits become obvious. Specifically, the Virial method does not adequately model the inflection that occurs in the isotherm data. As a result, the calculated isosteric heat of adsorption is under-estimated at ambient pressures.
a0=-3158(-3170,-3145)
a1=80.99(69.66,92.31)
a2=-18.49(-28.37,-8.606)
a3=2.663(-2.991,8.318)
a4=-0.06997(-1.439,1.299)
a5=-0.002171(-0.1199,0.1156)
b0=15.83(15.79,15.87)
b1=0.02755(-0.005748,0.06085)

Goodness of fit:
SSE: 0.0002938
R-square: 1
Adjusted R-square: 1
RMSE: 0.003129

a0=-3095(-3112,-3079)
a1=80.12(63.21,97.03)
a2=2.652(-14.69,19.99)
a3=-8.438(-19.58,2.705)
a4=2.409(-0.6235,5.442)
a5=-0.1913(-0.4851,0.1024)
b0=15.83(15.79,15.87)
b1=0.02755(-0.005748,0.06085)

Goodness of fit:
SSE: 0.0005482
R-square: 1
Adjusted R-square: 1
RMSE: 0.003129
**Goodness of fit:**

- SSE: 0.000243
- R-square: 1
- Adjusted R-square: 1
- RMSE: 0.002846

**Goodness of fit:**

- SSE: 0.0006986
- R-square: 1
- Adjusted R-square: 1
- RMSE: 0.002846
Fig. S13 The Isosteric Heats of Adsorption Calculations in CO$_2$ ($Q_{st}$) of Li-MOF-5 series

References