Measure of the heat of adsorption of hydrogen in microporous high-surface-area materials

Introduction: Microporous high-surface-area materials are a promising solution for hydrogen storage. They allow a high hydrogen uptake at high pressure and cryogenic temperature, typically at 77 K. But these materials can have complex behavior in the intermediate pressure range and with increasing temperature. To quantify this effect, knowledge of the isosteric heat of adsorption is essential. This determination requires good control of intermediate pressure and temperature. Typically, the isosteric heat of adsorption is calculated from the adsorption isotherms measured at 77 K and 87 K since these temperatures can easily be realized with liquid nitrogen and liquid argon, respectively. But using the PCTPro-2000 with the Microdoser attachment and a precise temperature control, a much wider range of pressure and temperature can be used, allowing a better accuracy for the determination of the heat of adsorption.

Results

The obtained PCT isotherms for each sample (An example is given on fig. 1 for the MOF Cu-BTC) can be normalized (fig 2.) to the hydrogen uptake value obtained at 20 bar and 77 K and then the isosteric heat of adsorption can be calculated with a good accuracy in a wide range of surface coverage (see next page).

Experimental

Two activated carbon (Norit R0.8 and Takeda 4A) and four metal-organic framework (MOF-5, Cu-BTC, MIL-53 and MIL-101) were investigated with the PCTPro-2000 to obtain the hydrogen PCT isotherms at different temperatures.

Results

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Results
From the isotherms measured at different temperatures the isosteric heat of adsorption can be determined for each material. It depends on the surface coverage $\theta$ following the equation:

$$\Delta H = -R \left[ \frac{\partial \ln(P)}{\partial (T^{-1})} \right]_{\theta}$$

where $R$ is the gas constant, $P$ the pressure and $T$ the temperature. The average isosteric heat of adsorption is given in the table 1. A high isosteric heat of adsorption leads to a high hydrogen uptake at low pressures. Furthermore, the temperature dependence of the hydrogen uptake is governed by the isosteric heat of adsorption (fig 3).

We can retain that:
- The slope of those isobars varies strongly with the isosteric heat of adsorption.
- A higher isosteric heat of adsorption means lower temperature dependence and therefore a higher relative uptake at elevated temperatures.

![Fig. 3: Isobars of hydrogen uptake at 20 bar for Takeda 4A (●), Norit R0.8 (■), MIL-101 (▲), and MOF-5 (▲).](image)


<table>
<thead>
<tr>
<th>Material</th>
<th>Isosteric heat of adsorption</th>
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</thead>
<tbody>
<tr>
<td>MOF-5</td>
<td>4.0 kJmol⁻¹</td>
</tr>
<tr>
<td>Cu-BTC</td>
<td>5.0 kJmol⁻¹</td>
</tr>
<tr>
<td>MIL-53</td>
<td>5.6 kJmol⁻¹</td>
</tr>
<tr>
<td>MIL-101</td>
<td>4.3 kJmol⁻¹</td>
</tr>
<tr>
<td>Norit R0.8</td>
<td>5.0 kJmol⁻¹</td>
</tr>
<tr>
<td>Takeda 4A</td>
<td>5.7 kJmol⁻¹</td>
</tr>
</tbody>
</table>

Table 1: Average isosteric heat of adsorption

Conclusion
This example demonstrates the improvement in measurement possibilities that the PCTPro-2000 with the Microdoser attachment permits. The high accuracy and precise temperature control of the PCTPro-2000 in physisorption studies over a wide range of pressure and temperature can be employed to obtain unique new information from PCT isotherms.