UNIQUE COUPLING BETWEEN µDSC AND VOLUMETRY

CO$_2$ ADSORPTION ON BASOLITE C300 STUDIED BY COUPLED VOLUMETRY - MDS

Metal-organic frameworks (MOFs) offer an advantage over other classical porous materials (activated carbon, zeolithes) because their properties can be tailored for specific applications. Today these structures are envisaged for multiple applications in gas adsorption, like hydrogen storage, selective adsorption of CO$_2$ against CH$_4$, CO$_2$ against H$_2$. The Cu-BTC (fig 2.) is chosen as a example of Metal Organic Framework that is available commercially to demonstrate adsorption studied by Sievert's technique and heat flow calorimetry.
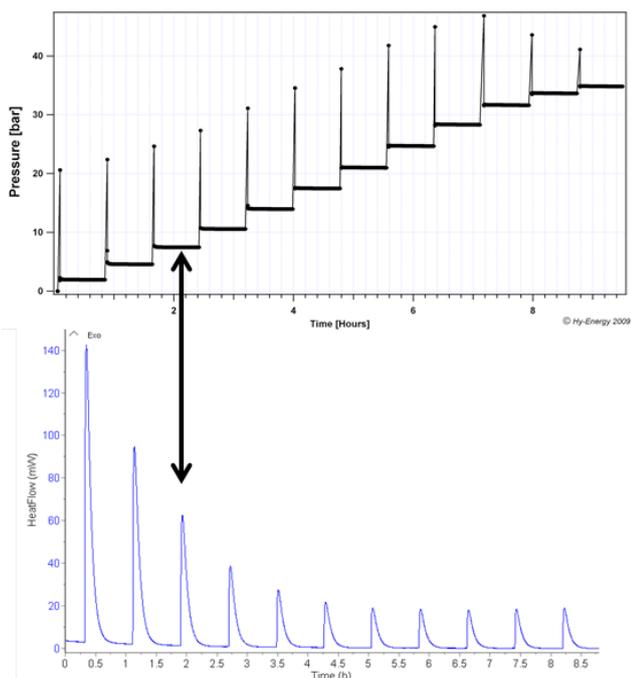

Figure 1. Up: Pressure versus time during a CO$_2$ adsorption experiment. At the beginning of each aliquot, the step is the measurement of the pressure in the manifold. Down: Calorimetric Heat Flow signal versus time. Each exothermic peak corresponds to the adsorption of a gas dose.
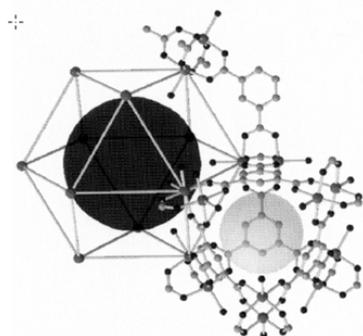
EXPERIMENTAL

CO2 adsorption into Basolite C300 was measured at -20°C, 30°C and 50°C using a PCTPro-E&E Sievert's apparatus coupled with a µDSC7 evo. Gas density temperature correction was performed by measuring the apparent free gas volume at these temperatures.

Understanding the thermodynamics of the adsorption is essential for the practical application and among all the enthalpy of adsorption (or desorption) it is a key parameter.

There are two ways to determine this enthalpy:

- The first one is an indirect method, where the enthalpy is derived from adsorption isotherms at different temperatures.

- The second one is a direct method, where the enthalpy is measured via a calorimetric technique. The biggest disadvantage of this technique is that it gives a result per mole of solid sample and not per mole of gas.

The combination of manometric technique (to quantify the amount of hydrogen absorbed/released) and calorimetry overcomes this issue and the direct measurement of enthalpy of formation per mole of gas is presented here (figure 1.).

Figure 2. Basolite C300 Cu-BTC

µDSC7 evo
-45°C to 120°C

KEY WORDS
ADSORPTION
CO$_2$
MOFS
VOLUMETRY
CALORIMETRY

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RESULTS AND CONCLUSIONS

Coupling allows the access to a full characterization of the adsorption: adsorption isotherms (fig 3.), integral heats of adsorption (fig 4.), isoteric heat of adsorption (fig 5.), differential heat of adsorption as a function of the adsorbed amounts (fig 6.).

The isosteric heat of adsorption is obtained by indirect methods by using the isotherms at different temperature. It gives the heat of adsorption at a specific coverage. It is obtained according to:

$$q_{st} = -RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_\theta$$

The differential heat of adsorption is the energy release during the adsorption for a infinitely small quantity of adsorbent. It depends on the adsorbed quantity of the gas. Practically this value is very important. It is this value that is used for the calculation of the sorption installations.

$$q_{diff} = \frac{\partial q_{int}}{\partial n^a}$$

The PCTPro and µDSC7 evo combination is an ideal technique for the detailed characterization of high surface area materials used in gas sorption. The ease of use and the temperature and pressure ranges are perfect for this type of material application and in particular in the case of CO_2 sorption studies.
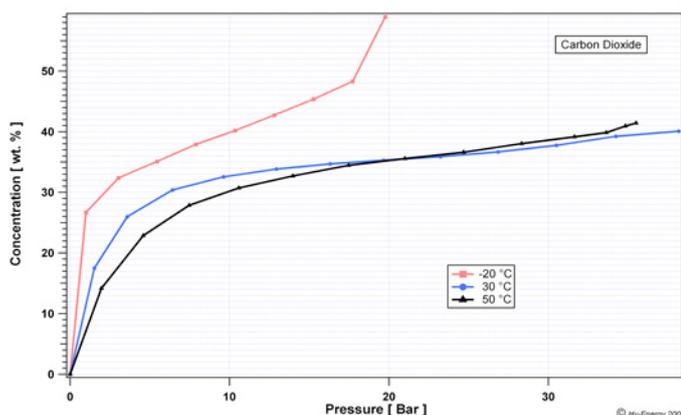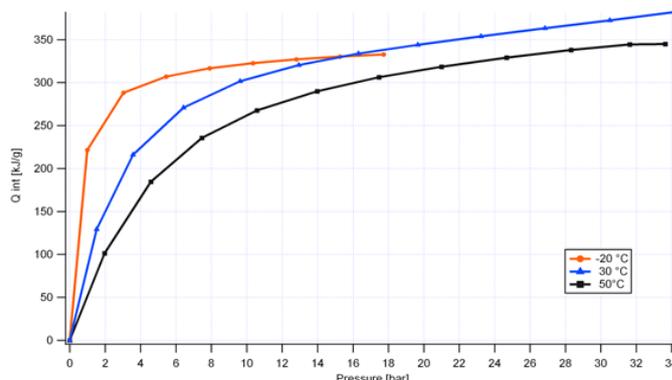

Figure 4. Total heat isotherms at -20, 30, 50 °C. It is the sum of all heat of adsorption versus pressure 30, 50 °C

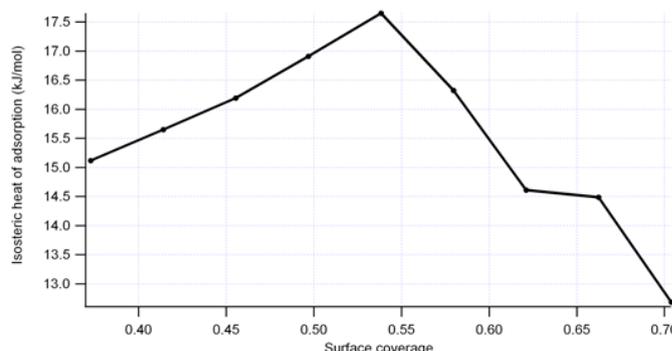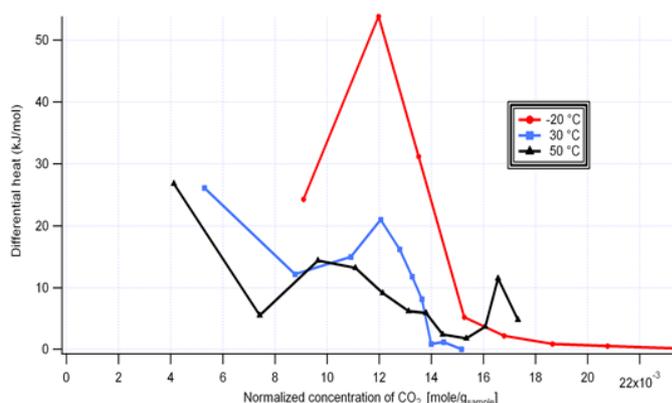Figure 5. Isosteric heat of adsorption versus surface coverage

Figure 6. Differential heat of adsorption versus the ormalized CO_2 concentration

Figure 3. CO_2 adsorption isotherms at-20, 30, 50 °C

PCTPro
-260°C to 500°C

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