Experimental report

17/10/2023

Proposal:	**1-04-242**	**Council:**	10/2022
Title:	Hydrogen storage mechanisms in disordered nanoporous carbons studied by small- and wide-angle neutron scattering		
Research area:	Physics		

This proposal is a new proposal

Main proposer:	**Sebastian STOCK**
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Samples: nanoporous carbon

Instrument	Requested days	Allocated days	From	To
D16	7	4	30/05/2023	06/06/2023
D4	5	0		

Abstract:

In this proposal we plan to study the hydrogen adsorption in activated carbons in-situ from 100 mbar up to 20 bar at a temperature relevant for cryogenic gas storage applications (77 K). Experiments will be performed at D16 and D4 by employing the gas sorption analyzer provided by the ILL SANE. Contrast variation by using hydrogen (H2), deuterium (D2), and a zero scattering-length H2/D2 gas mixture will allow to separate local contrast effects (induced by the adsorption and densification of hydrogen within the pore space) and considering also potential isotope effects and pore volume changes.

Experimental Report for Proposal 1-04-242

Hydrogen storage mechanisms in disordered nanoporous carbons studied by small and wide-angle neutron scattering

(30.05.-06.06.2023, D16)

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Aim of the experiment:

In previous experiments conducted at the D16 instrument (proposal 1-04-218 and 1-04-235) the hydrogen (H_2) and deuterium (D_2) adsorption in nanoporous activated carbons up to 30 bar and different (cryogenic) temperatures revealed the importance of narrow micropores for highest storage capability. The aim of this follow-up experiment was to:

1) Complete the missing data matrix and repeat some of the already performed experiments at D16 to demonstrate reproducibility.
2) Investigate one of the previous carbons (ACC) after surface chemical treatment (i.e. changed surface chemistry, but exactly the same pore structure)
3) Employ a new sample preparation technique that allows quantitative separation of coherent and incoherent scattering.
4) Extend the q-range up to 20 Å^{-1} to obtain radial distribution functions of the adsorbate and the adsorbent.

The previous experiments with the ACC material have been meanwhile summarized in a publication which is submitted. The main results from our previous SANS experiments at D16 for different materials (see reports **1-04-218 and 1-04-235**) was that for pressures of up to 1 bar at application relevant temperatures around 77 K only very small pores of ≈ 6-8 Å size (so called ultramicropores) are occupied with a highly densified adsorbate phase. The density in the smallest pores is approaching or even exceeding the bulk solid density [1], whereas in larger pores the gas only starts to noticeable densify at pressures well above one bar. The chemical treatment of the ACC material before the experiment did not result in a change of surface chemistry, thus we decided to investigate two new nanoporous carbon materials

Experimental details:

A commercially available high surface area carbon (Maxsorb) showing one of the highest reported hydrogen uptakes (~ 4.8 wt% at 77 K and 40 bar) [2], and an ordered mesoporous carbon (soft templated carbon – STC) with some small amount of microporosity [3], were investigated. With the new detector set-up at D16 a wide q-range up to 2.5 Å^{-1} could be covered, revealing the carbon 002 stacking peak and the structure factor peak from the adsorbate. Facilitating the D4 instrument to extend the q-range up to 20 Å^{-1} was not possible so far, since the corresponding proposal was rejected.

The experiments were conducted using the Hidden Isochema gas sorption analyzer available at the ILL at various pressure points up to 50 bar (see Figs. 1 and 2) and temperatures down to 20 K using H_2 and D_2. The samples were degassed at 250 °C under vacuum and placed in a custom-machined aluminum cell. To ensure stable powder density throughout the experiments the updated sample cell employs a filter gasket to densify the otherwise loose powder.

The cell volume and skeletal density of the sample were determined using helium pycnometry. The neutron scattering signal at D16 was recorded at 2 detector positions using a wavelength of 4.47 Å, which resulted in a covered Q-range of 0.03 – 2.5 Å^{-1}. Sample transmission at each pressure point, together with measurements of the background signal and a vanadium standard was used for data correction and calibration.

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[1] Experimental Team
[2] Local Contact
[3] Supervision

Collected data and results:

In Fig. 1 (a) the scattering curves of the Maxsorb sample at different H_2 loadings at 77 K up to 50 bar are shown. Slight changes in the intensity at the lowest recorded scattering vector values (< 0.06 $Å^{-1}$) can be attributed to an overall change in the scattering length of the micrometer- sized carbon powder particles, when H_2 or D_2 (Fig. 1 (b)) is adsorbed in the pore space. In the mid q-regime (> 0.1 $Å^{-1}$) the intensity with increasing amount adsorbed is decreasing up to 1000 mbar, which can be explained by filling of the smallest pores. When the equilibrium gas pressure reaches around 5 bar the intensity is increasing as also the larger micro and small mesopores are gradually filled. The increase in intensity, especially in the q-range > 0.4 $Å^{-1}$ can be explained by the high incoherent scattering contribution of H_2. In case of D_2 adsorption the contrast scenario is reversed, as H_2 has a negative scattering length and D_2 has a positive one. The highly disordered nature of carbon structure of this sample is reflected in the absence of a clear (002)-stacking reflection, usually visible around 1.7 $Å^{-1}$. In figure 1 (b) a clear peak is arising with increasing gas pressure, which we attribute to D_2-D_2 distance correlations. The increase of this peak is correlated to the amount of gas present in the pore space and partly due to the increasing coherent and incoherent scattering contribution of D_2. After separation of the coherent and incoherent scattering contributions, a detailed analysis of the adsorbate density within the pore space will be performed. From those two data sets, valuable information about the pore filling mechanism at technical relevant pressures and temperatures can be drawn.

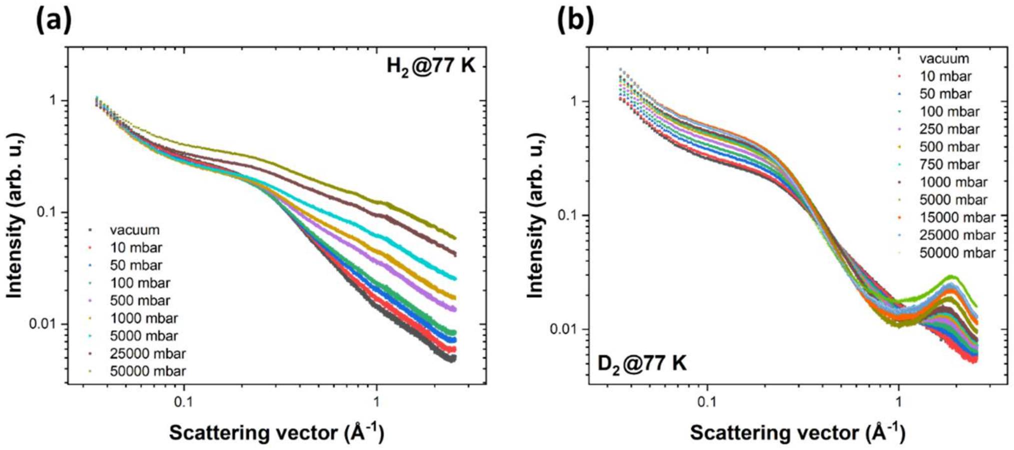

Fig. 1. Data collected for the Maxsorb sample: a) SANS curves at different H_2 pressures up to 50 bar, b) SANS curves at different D_2 pressures up to 50 bar

In Figs. 2 (a) and (b) the scattering signals for D_2 adsorption at 23 and 77 K of the STC material are shown, respectively. The Bragg-peaks around 0.07 and 0.12 $Å^{-1}$ arise from the hexagonally arranged cylindrical mesopores, whereas the small hump around 0.3 $Å^{-1}$ can be attributed to the micropores, believed to be embedded within the mesopore walls.

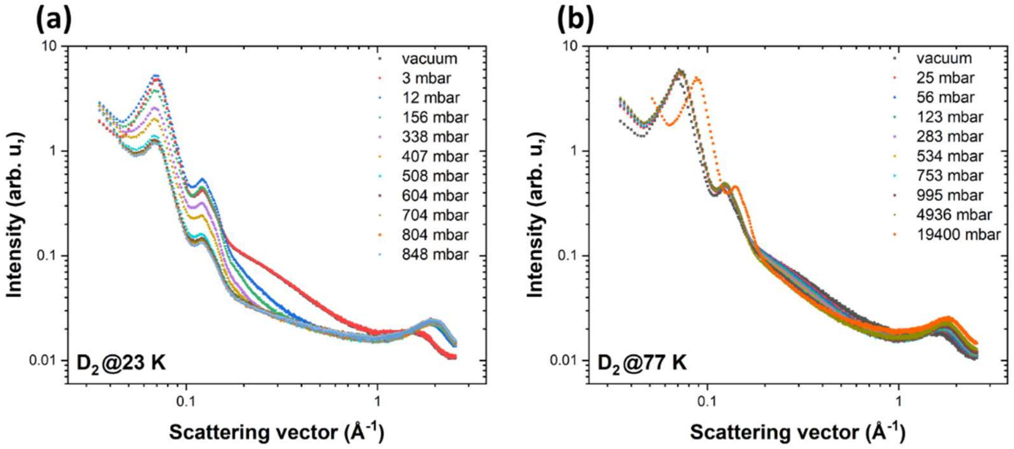

Fig. 2.: Data collected for the STC sample: a) SANS curves at different D_2 at 23 K and pressures up to 900 mbar, b) SANS curves at 77K and different D_2 pressures up to 20 bar

At the boiling point of D_2 the micropore filling is already completed at lowest gas pressures > 10 mbar and no further intensity change in the scattering vector range around 1 $Å^{-1}$ can be seen. From this we conclude that the gas density within this pore size regime has already reached a density as high as to match the scattering length density of the carbon matrix. At pressures around 12 mbar the mesopore scattering contribution is increasing compared to the sample under vacuum. This is expected as the mesopores remain unfilled. For higher pressures a decrease in peak intensity is noticeable relating to the filling of the mesopores with a dense adsorbate phase, to the point where pore condensation is occurring. In this sample the (002)-stacking reflection is more pronounced as compared to the Maxsorb sample, yet the same D_2-D_2-correlation peak can be seen. At 23 K this peak seems not to further increase, which hints towards that a maximum packing density within micropore confinement is already reached at lowest pressure. In Fig.2 (b) the scattering data of the STC material with different D_2 loadings at 77 K are shown. Here the decrease of intensity in the micropore regime is not as pronounced as at lower temperatures, hinting towards lower adsorbate density. The D_2-D_2 correlation peak is changing with higher gas pressures and the peak center is shifted towards higher scattering vector values. The mesopore scattering contribution is slightly increasing at higher D_2 loadings, which hints towards a low adsorbate density within these pores. At the highest recorded pressure of around 20 bar, the peaks are shifted towards higher q-values.

Further experimental investigations and data analysis:

The STC model material gives rise to a clear separation of the meso- and micropore scattering, which helps to understand the pore filling mechanism in more detail. A similar material with higher volume fraction of micropores was recently investigated using quasi-elastic neutron scattering (QENS) at IN16b (proposal 6-07-102 and the respective report) and is intended to be measured also by inelastic neutron scattering (see also proposal 7-05-603). From those experiment details about adsorbate dynamics within nanopore confinement [4] and the ortho-to-para H_2 transition [5], as well as differences in adsorption behavior can be elucidated. From SANS we can identify the position of the hydrogen molecules within the porous structure, thus generating a holistic picture of the effects of confinement on the adsorbate density as well as the dynamics.

References:

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