Experimental report

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Proposal: 6-07-107 **Council:** 10/2022

Title: Confined crystalline D2 phase in ordered microporous zeolite-templated carbons

Research area: Materials

This proposal is a new proposal

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Samples: zeolite-templated carbon (pure carbon)
zeolite-templated carbon (pure carbon) plus H2

Instrument	Requested days	Allocated days	From	To
D20	4	4	30/03/2023	04/04/2023

Abstract:

Development of high efficiency and safe hydrogen storage materials is vital for the move towards a hydrogen based greenhouse gas emission free and sustainable economy. Zeolite-templated carbons are a highly potential hydrogen storage materials. In addition, the highly ordered microporous structure of zeolite-templated carbons (ZTC) is excellent as a model material to investigate the hydrogen-carbon interactions in pores with specific sizes, geometries, and also chemical makeups. In this study we will determine the influence of the ordered microporus carbon structure on the D2 crystallisation. For this three ZTCs are used, where the influence of N-functionalisation is investigated via two samples, which have been prepared to contain N-functionalisations. The adsorbent porosity influence on melting temperature and the crystalline fine-structure will be determined. This study is planned in tandem with SANS and QENS measurements to form a complete picture about the H2-carbon interactions in case of N-functionalised ZTCs.

Confined crystalline D_2 phase in ordered microporous zeolite-templated carbons

Scientific background and aim of this experiment

Adsorption of H_2 in high surface area microporous carbon materials for hydrogen storage applications has been extensively investigated [1,2,3,4]. An important aspect of fully understanding H_2 adsorption in microporous carbon materials is investigating the formation of ordered structures at low temperatures (≤ 77 K) and the role of different-sized, shaped, and functionalized pores in forming confined crystalline phases [4,5,6,7]. The formation of highly dense adsorbed H_2 phases in micropores has been shown previously, where the adsorbed phase was shown to be denser than liquid H_2 [7,8,9]. In addition, the influence of micropores on the formation of different crystalline phases of H_2 under high H_2 pressures (> 20 MPa) and the retainment of the solid H_2 phase at higher temperatures has been shown recently by Terry et al. [7]. Thus, in this experiment, we investigated the role of N-functionalisation and ordered microporous structures on the formation of an ordered adsorbed D_2 phase. For this, zeolite-templated carbons (ZTCs) were used as robust model materials for their highly ordered pore structure with well-defined pore widths and high specific surface areas (up to 3100 $m^2 g^{-1}$) and the possibility to control N-heteroatom functionalization.

Experimental routines:

Neutron diffraction measurements were performed on three ZTC materials: Bulk carbon ZTC, ZTC1, and two N-heteroatom active sites containing ZTCs, ZTC2 and ZTC3. All ZTCs were degassed before measurement, and neutrons with a wavelength of 1.54 Å were used. The used experimental routines are brought in Table 1.

Table 1. Used experimental routine

ZTC1	ZTC2	Empty sample holders	ZTC3
Degassing at RT	Degassing at RT	Degassing at RT	Degassing at RT
Cooling to 10 K	Cooling to 10 K	Cooling to 10 K	Cooling to 10 K
10 K and 77 K full diffractogram scans	10 K and 77 K 2theta scans	2theta scans with increased Ts up to 77 K	10 K and 77 K 2theta scans
Dosing with 1.28 bar of D_2 at 77 K	Dosing with 0.82 bar of D_2 at 77 K		Dosing with 1.82 bar of D_2 at 77 K
Cooling to 10 K	Cooling to 10 K		Cooling to 10 K
2theta scans with increased Ts up to 77 K	2theta scans with increased Ts up to 77 K		2theta scans with increased Ts up to 77 K

Experimental results:

The scattering data was subtracted with that of the degassed sample holder to eliminate the intense diffraction peaks from the Al sample holder. This caused slight scattering anomalies near Q regions of 3.1 $Å^{-1}$, 4.4 $Å^{-1}$, and others (Figure 1a,b,c). Degassed ZTCs exhibited typical scattering patterns of non-graphitic carbon material with clear (100)/(101) and (110) diffraction peaks belonging to graphitic carbon (Figure 1a). With the application of D_2 loading at 77 K, an intense and diffuse

diffraction peak appeared near Q = 2.0 Å^{-1}, corresponding to a *d*-spacing of around 3.3 Å. The diffraction peaks decreased in intensity and the *d*-spacing value increased with increased temperature (Figure 2). This is indicative that the measured diffraction peak is caused by the ordered adsorbed D_2 phase, which desorbs upon heating and, thus causes a decrease in the integrated peak intensity.

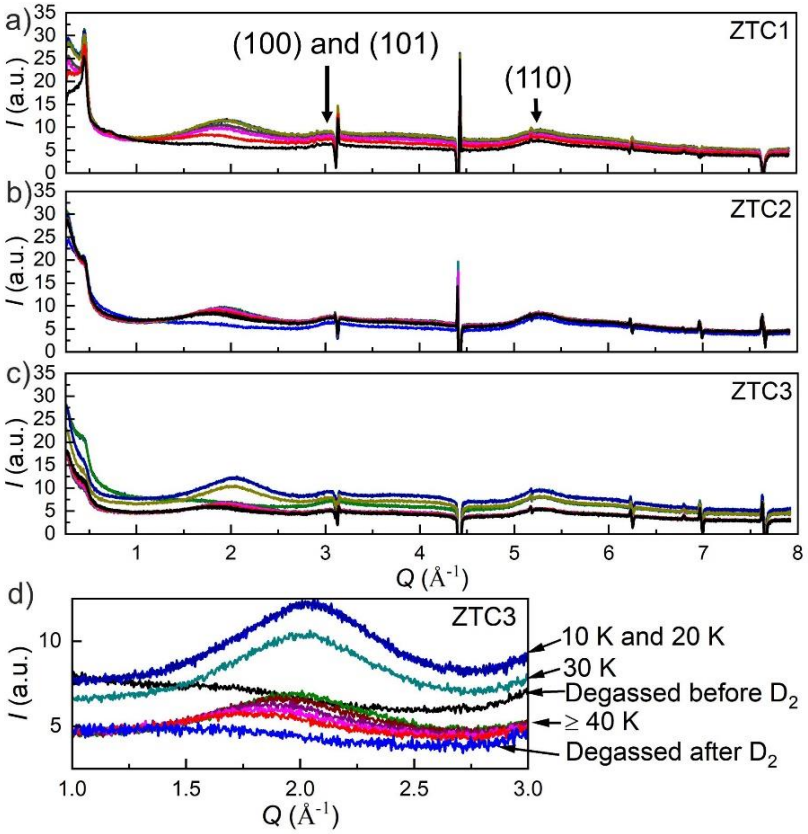

Figure 1. Diffraction patterns of ZTC1 (a), ZTC2 (b), and ZTC3 (c) in degassed form (lowest intensity lines) and under D_2 loading at different temperatures. The diffraction pattern of the sample holder was subtracted from all diffraction patterns and this caused anomalous negative peaks around Q of 3.1 Å^{-1}, 4.4 Å^{-1} etc. A zoom-in of the formed diffraction peak at around Q = 2 Å^{-1} is presented for ZTC3 (d).

Further plans:

A manuscript will be prepared based on the obtained results after the paper outlining the synthesis of the used ZTC has been published (is currently in the works). Based on the results from ZTC3, experiments utilizing polarized neutron analysis are planned to separate the coherent and incoherent part of scattering from H_2 to be able to determine exactly which part if the formation of the wide diffraction peak is caused by the adsorbed D_2 phase or changes in the structure of the ZTC.

References:

[1] M.G. Nijkamp et al., Appl Phys A 72 (2001a) 619–623.
[2] G. Yushin et al., Advanced Functional Materials 16 (2006b) 2288–2293.
[3] N. Texier-Mandoki et al., Carbon 42 (2004c) 2744–2747.
[4] R. Härmas et al., Carbon 155 (2019d) 122–128.
[5] M. Koppel et al., Carbon 197 (2022e) 359–367.
[6] Y. Xia et al., Carbon 49 (2011f) 844–853.
[7] L.R. Terry et al., Nanoscale 14 (2022g) 7250–7261.
[8] C.I. Contescu et al., Carbon 50 (2012h) 1071–1082.
[9] J. Bahadur et al., Carbon 117 (2017i) 383–392.

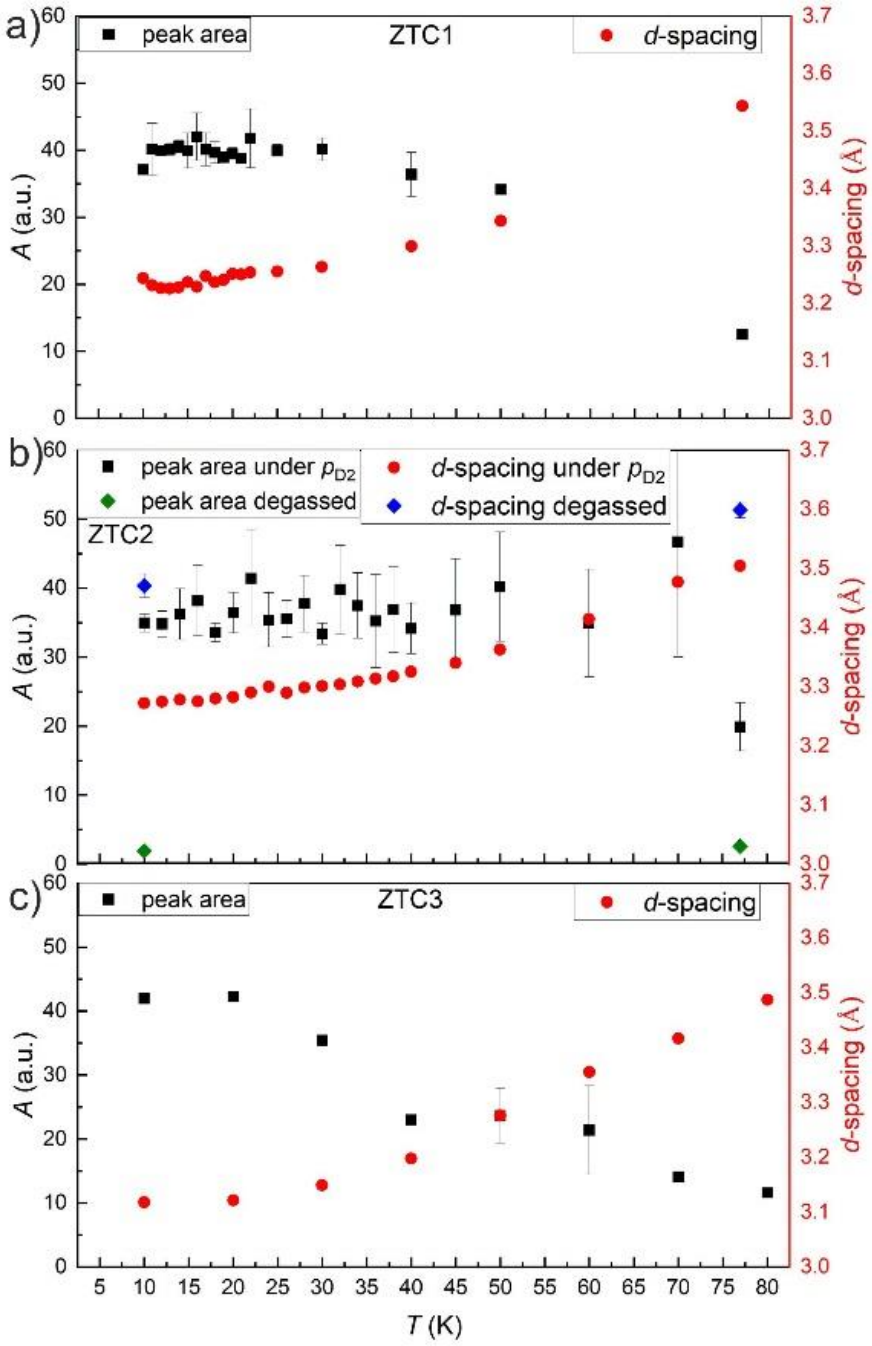

Figure 2. Integrated areas and *d*-spacings of the diffuse diffraction peak at around Q = 2 $Å^{-1}$ for ZTC1 (a), ZTC2 (b), and ZTC3 (c). In case of ZTC2 (b), the integrated peak area (green symbols) and *d*-spacing (blue symbols) of the (002) diffraction peak from graphite of degassed ZTC2 are shown for comparison.