Experimental report

02/09/2022

Proposal: **EASY-970** **Council:** 4/2021

Title: Unrevealing the meso- and micro-structure of activated carbons for catalysis

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Andrea PIOVANO**

Experimental team: Alberto RICCHEBUONO

Local contacts: Ralf SCHWEINS

Samples: C

Instrument	Requested days	Allocated days	From	To
D11	6	6	06/09/2021	07/09/2021

Abstract:

Carbonaceous materials cover a very large family of structures and textures that span a wide range of unique chemical and physical properties. Activated carbons are used in a large number of applications and have been successfully used as support for catalysts or as catalysts on their own.

The catalytic properties of different carbons are strongly influenced by macro- and micro-structural features, that include the specific surface area, surface chemistry, morphology as well as their pore structure. The disordered character and the difficulties of reliably uncoupling pore size and pore accessibility, still represent a characterization challenge for carbons. In particular, microstructural features of carbonaceous materials are locked by the limitations of conventional analytical techniques. The result is an incomplete or simplified description of carbon structure and microstructure. Traditional models are based on an assembly of pseudo graphitic nanocrystals. However, alternative models have recently been proposed based on curved layers.

In this proposal, we intend to use of Small Angle Neutron Scattering to study the structure of two types of carbons at multiple length scales.

Experimental Report EASY-970

A SANS study of the structure of activated carbons for catalysis from the nano- to the meso-scale

1. Introduction

In the past, our team's research was involved in the deep characterization of the physical-chemical properties of several activated carbons differing for their origin (wood or peat) and activation process (by steam or by chemical methods), as well as on the investigation of catalysts obtained by supporting Pd and Pt nanoparticles (NPs) on said activated carbons. By coupling an unusually high number of techniques, we were able to shed light on their molecular level structure and surface properties, and to relate some of these properties to their catalytic activity.[1–5] The characterization of the inherently complex carbon porosity is the last obstacle preventing us from a complete knowledge about these samples. We decided to carry out a SANS experiment to fulfil this task for two main reasons: 1) unlike X-rays, neutrons allow to employ the technique of contrast matching to access important additional information about the porosity of the materials; 2) neutrons show a better sensitivity than X-rays for the main atoms constituting activated carbons (H and C) with respect to the supported metals, allowing to detect possible morphology changes induced in the carbon material by the deposition of metal NPs.

The application of SANS to the study of pores in activated carbons is not trivial.[6] Thus, we conceived this experiment as an explorative step, carried out without any contrast agent, aimed to:

- Pointing out qualitative differences in the SANS patterns of our samples.
- Testing the experimental procedure, to identify critical points to be resolved before the next experiments.
- Generating a preliminary set of data to rely on for setting up an efficient experiment with a contrast matching agent.

2. Experimental

During the experiment we analysed three samples of wood origin: Cch (chemically activated with H_3PO_4), Cwa (physically activated with steam) and Pd/Cwa (prepared by dispersing Pd NPs on Cwa by deposition-precipitation).[7] The three samples were activated in the laboratories of the University of Turin by heating at 120 °C, under dynamic vacuum (final pressure $5*10^{-4}$ mbar). The procedure, featuring a rather low activation temperature, was intended to remove from the surface as much physisorbed water as possible, without promoting the sintering of the Pd NPs. The activated samples were packed within a glovebox and delivered to ILL. There, they were inserted into sealed flat aluminium cells inside the glovebox.

Each sample, as well as the background, was analysed at three different distances from the detector: 1.7 m, 8 m, 38 m. To scan the large Q range ranging from around 1 to around 0.0001 $Å^{-1}$, we planned to collect SANS patterns setting the neutron beam at two different wavelengths: 6 and 13 Å.

3. Results and discussion

A correct acquisition of the scattered neutrons for λ = 13 Å was hampered by the presence of multiple scattering, indicating that the chosen sample thickness (3 mm) was excessive for this experiment.

The presence of multiple scattering is clearly detectable from the plots in Figure 1A, since it is responsible for the mismatch between the data points collected for λ = 13 Å (from 0.001 to around 0.003 $Å^{-1}$) and λ = 6 Å. If the samples are too thick, multiple scattering will affect the whole Q range, for both the chosen wavelengths, nonetheless, this phenomenon is less relevant as Q increases or as λ gets shorter. For this reason, data collected at low Q with λ = 13 Å are completely unreliable, while data collected with λ = 6 Å (Figure 1B), especially in the range between 0.01 and 1 $Å^{-1}$ can still serve as a basis for qualitative discussions about the information SANS can provide about these samples.

Before discussing directly the SANS patterns collected in this experiment, it is worth reasoning about the dimensions of the carbon domains and the pores present in the samples, aiming to locate the contribution

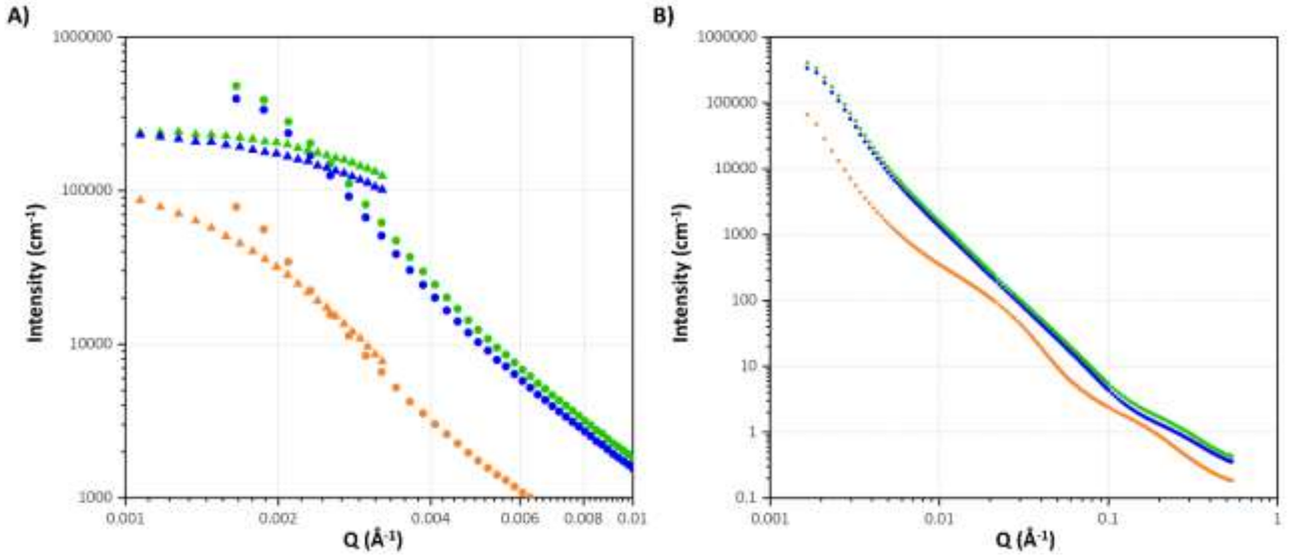

Figure 1. The three SANS pattern collected during the experiment are presented for Cch (orange), Cwa (blue) and Pd/Cwa (green). A) Zoom of the low Q region in which the mismatch between points collected for λ = 6 Å (dots) and λ = 13 Å (triangles) is easily noticeable. B) Data points collected for λ = 6 Å.

of their form factor in the Q space. As a result of previous X-Rays Powder Diffraction measurements, we know that the average lateral dimension of the regular flat carbon domains is 12.5 Å for Cch and 16.5 Å for Cwa. The mesotructure of the carbon grains has been analysed with SEM surveys revealing particle of the order of 20 um to 200 um, showing however statistically smaller particles in the chemically activated carbon.[4] We then expect the microscopic structure of the carbon grains lying somewhere in between, but the actual average size and distribution is not yet known, while fall well in the range exploitable with SANS. Pore Size Distributions (PSDs) for Cch and Cwa were evaluated by applying Non-Local Density Functional Theory[8] to N_2 adsorption isotherms (see Figure 2). The two PSDs show that the dimension of the smallest nanopores (< 15 Å diameter) is comparable with the dimension of the carbon domains, allowing to confine the contribution of the form factor of both in the highest region of the scanned Q space (from around 0.1 Å^{-1} until above the presently collected range). From the isotherms we however evidence the presence of further micro and meso pores that cannot be clearly extracted from the NLDFT analysis.

The plots reported in Figure 1B show a few significant differences, which can be linked to morphological diversities in the samples. The SANS patterns collected for Cch and Cwa are completely different, suggesting that they exhibit two distinct morphologies on the micro and mesoscale. The diversity of the SANS patterns at high Q (greater than 0.1 Å^{-1}) could be the expression of the difference in the form factor

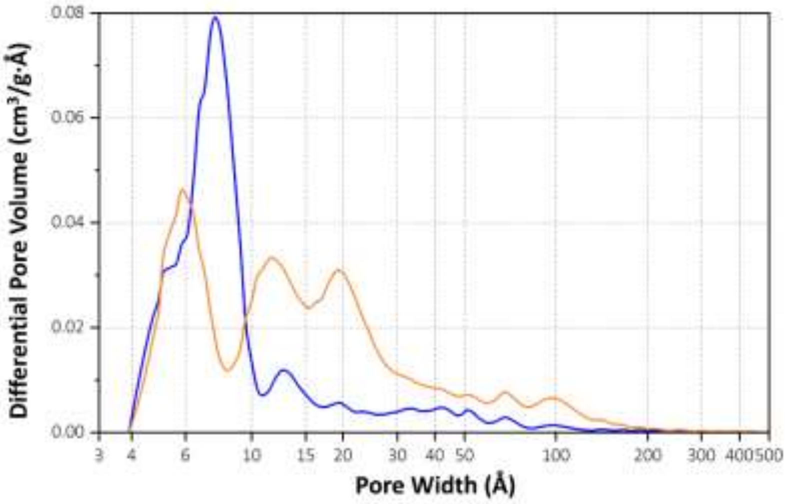

Figure 2. Unpublished PSDs evaluated by post-treating with NLDFT adsorption isotherms collected for N_2 at 77K. The employed NLDFT model assumes a slit shape for modelling the pores.

of the pores between Cch and Cwa. However, the fact that the contribution of the form factor of the carbon domains falls in the same region hampers further reasoning relying on these data. On the other hand, the differences between the two SANS patterns at lower Q (from 0.01 to 0.1 $Å^{-1}$), should represent a different form of organization of the larger micropores in space. Concerning the lowest Q range, it seems that neither Cwa nor Cch show to plateau until 0.002 $Å^{-1}$ (slight bending is probably due to multiple scattering). For a reliable analysis of our data, we then need to access the lowest possible range of available Q around 0.001 $Å^{-1}$. Also in this case, we cannot move forward with the discussion, since the contribution from pores cannot be separated from the one of grains of similar size without the employment of a contrast matching agent.

The difference between the SANS patterns collected for Cwa and Pd/Cwa is almost negligible for largest part of the scanned Q space. The only significant difference, albeit extremely small, is reported at high Q. This suggest that the deposition of Pd NPs can imply a tiny perturbation in the local structure of the carbon architecture, without influencing the organization on a larger scale.

4. Conclusion

The presented experiment was intended as a preliminary study, devoted to get familiar with the characterization of pores in carbons with SANS. As we planned, we were able to identify significant differences in the SANS patterns of Cwa and Cch, which means that they exhibit a different micro and mesostructure. On the other hand, the two similar patterns collected for Cwa and Pd/Cwa suggest that the deposition of the metal does not entail massive changes in the structure of the activated carbon. Even though the collected data are affected by multiple scattering, making them not completely reliable, this should not lead to consider this experiment as a failure. Since we were able to locate the reason of multiple scattering in the sample thickness, this information will be exploited for the next experiments: by preparing samples less than 1 mm thick, we will get rid of this complication.

As foreseen, relying on just one plot per sample collected in vacuum is not enough to fully access all the information we need about the spatial organization of all the different families of pores. However, relying on the acquired knowledge, we are planning a new and more sophisticated experiment. By employing D_2O as a contrast agent, we will try to disentangle this overlap of contribution and reach an exhaustive knowledge on the spatial organization of the pores in our activated carbons.

5. References

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