Experimental report

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Proposal: TEST-3271 **Council:** 4/2023

Title: Micropore structure of activated carbon of different origin

Research area: Chemistry

This proposal is a new proposal

Main proposer: Andrea PIOVANO

Experimental team: Andrea PIOVANO
Alberto RICCHEBUONO
Eleonora VOTTERO

Local contacts: Viviana CRISTIGLIO

Samples: activated carbon

Instrument	Requested days	Allocated days	From	To
D16	2	2	26/06/2023	28/06/2023

Abstract:

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.

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Micropore structure of activated carbons of different origin

1. Introduction

Activated carbons are extremely popular materials, widely employed as catalytic supports or catalysts on their own, adsorbents, storage materials and even components of electrochemical cells. Thanks to the activation process, carbons develop a series of pores, which remarkably increase their surface area. Our team's research has previously been involved in the characterization of the physical-chemical properties of several activated carbons of different 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]

However, the debate on their micro- and meso-structure and its impact on the activity of these materials is still open. The reason behind this open question lies in the highly disordered nature of these materials, coupled with the intrinsic limitations affecting routine techniques employed for their characterization. For example, inferring the Pore Size Distribution (PSD) from gas sorption measurements requires strong assumptions on the pore geometry, while conventional X-Rays Diffraction (XRD) is blind to the structural organization of these materials, lacking long-range order. In the last decade, the widely accepted model of activated carbons as an ensemble of cross-linked flat graphitic platelets, randomly oriented to create voids (i.e. micropores), has been widely questioned. The contribution of curved domains could be necessary to explain experimental data from several techniques. For example, the interpretation of the broadening of the XRD peaks in activated carbons as due to the crystallite size shrinking can be indeed combined with the presence of curved domains. Arising from the presence of non-hexagonal rings formed during the activation process, the contribution of curved layers could give the micropore structure a quite different look compared with the conventional model.

Given the limitations of conventional techniques, Small Angle Neutron Scattering (SANS) is generally known as suitable for accessing topological information at the required dimensional scale both for crystalline and amorphous samples. Moreover, employing neutrons has the unique advantage of (1) granting of high sensitivity for the main atoms constituting activated carbons (H and C) and (2) providing information about pore accessibility by gradually filling the pores with a contrast matching agent, like D_2O. Thus, relying on previously collected PSDs inferred from Ar sorption measurements, we carried out a SANS experiment with the aim of gathering information concerning:

- The PSD our samples independently for gas sorption, pointing out morphological differences among the analysed carbons.
- The spatial organization of the pores in the carbon matrix.
- The existence and abundance of curved carbon domains.
- The accessibility of the micropores thanks to contrast matching with D_2O.

2. Experimental

The experiments were focused on five samples (namely C_{ch}, C_{wa}, C_{pa}, $C_{wa\text{-}ox}$, $C_{ch\text{-}ox}$) of different origin and activation (see Table 1). Two of them were further oxidized with HNO_3. The porosity of the activated carbons was first characterized with Ar sorption in the laboratories of the University of Torino. PSDs were inferred for each sample with Non-local Density Functional Theory (NLDFT), with the scope of determining the total pore volume of the micropores. The five samples were activated in the same laboratories by heating at 120 °C under dynamic vacuum (final pressure 5 10^{-4} mbar), to remove from the surface as much physisorbed water as possible. The activated samples were transferred into a glovebox and divided into 4 aliquots. One aliquot was left as activated, while the three remaining ones were impregnated with a D_2O amount equal to 1/3, 2/3 and the totality of the micropore volume measured through Ar sorption. The such-prepared samples were inserted into quartz capillaries and sealed under N_2 with atmosphere with photo-crosslinking polymeric glue. Thanks to the knowledge acquired during the previous experiment EASY-

970, the thickness of the employed quartz capillaries was chosen as 2.0 mm to grant a good sensitivity while avoiding multiple scattering.

Table 1. Summary of the synthetic history of the analysed samples

	C_{wa}	C_{ch}	C_{pa}	$C_{wa\text{-}ox}$	$C_{ch\text{-}ox}$
Origin	wood	wood	peat	wood	wood
Activation	physical (steam)	chemical (H_3PO_4)	physical (steam)	physical (steam)	chemical (H_3PO_4)
Oxidation	no	no	no	yes	yes

Each sample, the empty cell and two references for data normalization (Vanadium and pure D_2O), were analysed positioning the detector at three different angles (γ) with respect to the incident monochromatic beam (λ = 4.503 Å). γ = 0° was employed to collect the transmitted intensity, while γ = 44° and γ = 90° were employed to collect the scattered intensity respectively in the low- and high-q regions. This experimental configuration allowed us to collect SANS patterns in a q region ranging from around 0.03 to 3 $Å^{-1}$.

3. Results and discussion

The Ar-PSDs inferred by means of NLDFT (Figure 1A) suggest that physically activated samples (C_{wa}, C_{pa}, $C_{wa\text{-}ox}$) present a greater fraction of nanopores (3 - 7 Å) with respect to chemically activated ones (C_{ch}, $C_{ch\text{-}ox}$), the latter featuring an important fraction of bigger pores (10 - 25 Å). Moreover, the Ar-PSDs of the oxidized samples ($C_{wa\text{-}ox}$, $C_{ch\text{-}ox}$) appear qualitatively similar to the PSDs of the non-oxidized ones (C_{wa}, C_{ch}). To aid the interpretation, the SANS patterns of the same set of samples under bare N_2 atmosphere (Figure 1B) can be divided approximately into three different q regions:

- High q region (approx. 3 $Å^{-1}$ > q > 1 $Å^{-1}$), featuring a diffraction peak ascribable to the distance between stacked carbon layers.
- Medium q region (approx. 1 $Å^{-1}$ > q > 0.1 $Å^{-1}$), featuring a bump caused by carbon microporosity.
- Low q region (approx. 0.1 $Å^{-1}$ > q > 0.3 $Å^{-1}$), which slope around q^{-4} represents the Porod-like scattering of the macroscopic powder grains.[6]

Thanks to a first qualitative analysis, we observe that similarities and differences between samples deducible from Ar-PSDs (Figure 1A) are in excellent agreement with the information contained in the respective SANS patterns (Figure 1B). Samples featuring the same activation procedure feature both similar PSDs and SANS patterns in the medium and low q region, while just sample sharing the same activation and origin present analogue features also in the high q region. Moreover, the medium q region contribution of the micropores of chemically activated samples occurs at lower q values with respect to the physically activated samples, in agreement with higher fraction of bigger micropores highlighted in C_{ch} and $C_{ch\text{-}ox}$ by the respective Ar-PSDs.

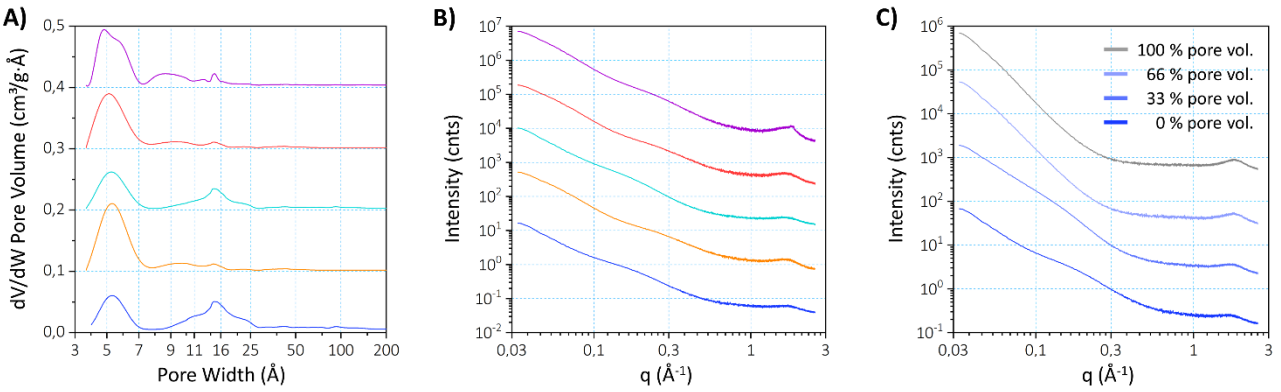

Figure 1. Ar-PSDs (A) and SANS patterns collected under bare N_2 atmosphere (B) for C_{ch} (blue), C_{wa} (orange), $C_{ch\text{-}ox}$ (cyan), $C_{wa\text{-}ox}$ (red), C_{pa} (magenta). C) SANS patterns of sample C_{ch} collected at different D_2O impregnation percentages, referred to the total pore volume. All plots are presented with an offset to simplify their interpretation.

SANS patterns at increasing D_2O impregnation levels were collected for each sample. As it is exemplified for C_{ch} in Figure 1C (the other samples present similar features), filling carbon pores with D_2O results in gradually wiping out the respective scattered intensity of the pores due to the similarity of the scattering length density (SLD) of D_2O with the SLD of the carbon matrix. From a qualitative analysis, it appears that the whole scattering contribution in the medium q region is suppressed at 100 % impregnation, which suggests that the samples do not present inaccessible pores.

4. Conclusion

With the presented experiments we have been able to collect SANS patterns for five activated carbons of different origin and activation at different D_2O impregnation levels. The presented qualitative analysis has already been able to testify the agreement between two completely independent techniques like SANS and Ar sorption NLDFT. Nonetheless, a huge amount of additional information is yet to be extracted by means of an accurate analysis of the SANS data, which will be performed in the following months. Ar sorption measurements have been able to provide us accurate PSDs, even though within the strong assumption of the slit-like pore shape. Moreover, these measurements are completely blind to the organization of the pores in space and their accessibility. By an accurate analysis of the collected SANS data, we will be able to complement Ar sorption with topological information and to point out the existence of curved domains. Extracting all these data from the SANS patterns will involve a delicate fitting procedure, devoted to separate and analyse the contributions of carbon particles, micropores and structural peaks of the carbon matrix. Since this will involve the employment of several fitting models, we are planning to check their performances *a posteriori* by performing a statistic analysis based on the Bayesian inference.

5. References

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