

CARBON POROSITY DEVELOPMENT VIA SMALL ANGLE SCATTERING

J. M. Calo[†], P.J. Hall, S. Brown, J. Fernandez, and M. Antxustegi[†]

Department of Pure and Applied Chemistry

University of Strathclyde, Glasgow G1 1XL, Scotland

[†]Chemical Engineering Program, Division of Engineering, Box D

Brown University, Providence, RI 02912, USA

Introduction

Small angle scattering (SAS) techniques represent an alternative to gas adsorption methods with a number of advantages. SAS is sensitive to both "closed" and "open" pores, and in many cases offers a more complete description of porosity. SAS can also be applied to "wet" samples. Both X-rays (SAXS) and neutrons (SANS) can be produced at suitable wavelengths for SAS.

Here we provide a summary of some selected results concerning the application of these techniques to porosity characterization in carbons and chars.

Experimental

SANS was performed at the small angle neutron diffractometer located at the Intense Pulsed Neutron Source (IPNS) of the Argonne National Laboratory [1], using 2 mm pathlength Suprasil cells. SAXS measurements were carried out with a Kratky camera mounted on a fully stabilized Phillips generator, Type PW 1010/1, operated at 40 kV and 20 mA. A Ni filter was used for the Cu- β radiation. Both entrance and counter slits had widths of 250 μ m. Carbon samples were loaded into 2 mm thick sample holders, 1 cm wide and 1.6 cm in height, covered with kapton film on both sides.

Results and Discussion

Three selected topics are briefly presented here: (1) SANS on a glassy carbon; (2) SANS on a Wyodak coal char; and (3) a comparison of SAXS and SANS data.

(1) SANS data were obtained for four phenolic resin samples burned-off to varying extents in oxygen at 470°C. For these data, the total scattering intensity *decreased* with increasing activation at low burn-offs, contrary to what is usually observed for most carbons and chars [2,3]. A conventional interpretation of these data would provide little or no indication of the pore opening process.

Contrast-matching SANS data were also obtained for the same samples. This was done by immersing the sample in a liquid with a neutron scattering cross section close to that of carbon; perdeuterated toluene in the current case. Filling the voids with the contrast matching solvent eliminates the scattering contribution from the "open" or "accessible" porosity. This means that the contrast-matched data are reflective of the "closed" or inaccessible porosity, while the difference in the scattering data between

the "dry" and contrast-matched ("wet") samples are indicative of the "open" or accessible porosity.

The "difference" scattering data for these same phenolic resin samples are presented in Figure 1. Unlike for the "dry" samples, these data now show the expected *increase* in scattering with activation at low burn-offs, especially with respect to the development of microporosity (i.e., at high q ; where $q = 4\pi \sin(\theta)/\lambda$ is the scattering wavevector).

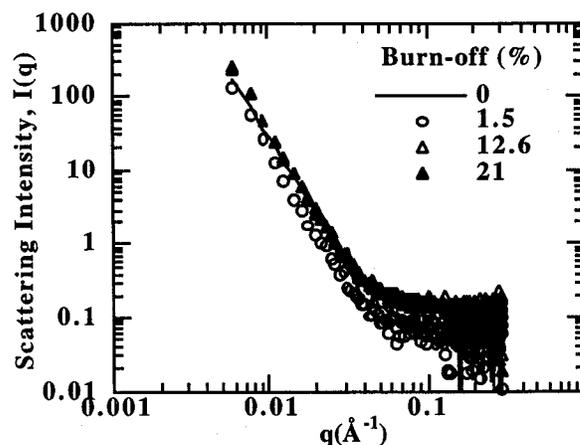


Figure 1. "Difference" SANS intensities from "dry" and contrast-matched phenolic resin char samples.

The behavior of this char is attributed to the selective burn-off of disordered carbon material at low levels of activation. Analysis of the SANS data has been used to find that this material exhibits a broad distribution of characteristic size up to about 300Å, with a mean *ca.* 102Å, which originally blocks access to almost the entire intrinsic underlying porosity. The distribution of intrinsic porosity was found to be well fit by a bimodal Schulz distribution of fully penetrable polydisperse spheres [4], comprised of a narrow distribution in the micropore size range with a mean of about 9.4Å, superimposed on another broad distribution of pore sizes. The primary effects of burn-off of this carbon material are progressive removal of the disordered carbon, resulting in the conversion of initially inaccessible to accessible porosity. There was no evidence of significant widening or alteration of the intrinsic underlying porosity, nor of the development of new porosity up to 21% burn-off.

(2) Figure 2 shows scattering intensity curves for six "dry" Wyodak coal [5] char samples burned-off to different extents in air at 400°C. As shown, the total scattering increases with activation up to 58% burn-off, whereupon it

then decreases at 68% burn-off. This is qualitatively similar to the behavior found for other carbons [2].

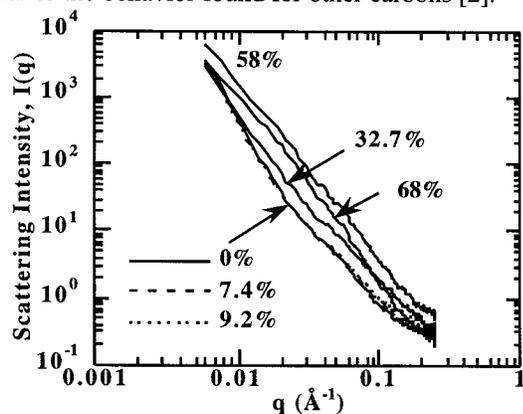


Figure 2. Neutron scattering intensities for Wyodak coal char activated to varying extents in air at 400°C.

However, Wyodak coal contains a significant amount of mineral matter 6.31% (as received). Following pyrolysis, the mineral matter content of the char increases to about 15.9% on a dry basis. In this case, SAXS was used to show that about half of the scattering exhibited by the contrast-matched unactivated char was due to mineral matter. In addition, it was shown that there was a significant amount of “closed” porosity present during the early stages of activation, which disappeared by 32.7% burn-off. Thus, in this case SANS gives additional information about pore development and the relative contribution of mineral matter, which is not possible using other porosity characterization techniques.

(3) In general, it is typically assumed that SAXS and SANS provide essentially the same information. However, the scattering mechanisms are completely different for the two types of subatomic particles. For SAXS, interactions with electrons are most important, whereas interactions with nuclei are more important for SANS.

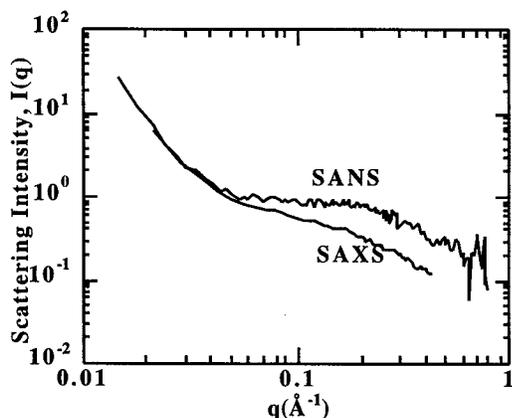


Figure 3. SANS and SAXS scattering intensities for a phenolic resin char.

In Figure 3 are presented SAXS and SANS data obtained for the same sample of phenolic resin char. As shown, the scattering intensity curves both exhibit the same power law behavior in the low q region, indicative of meso- and macroporosity of a fractal nature. The marked

upward deviation from the fractal behavior in both the SAXS and SANS data for $q > 0.03 \text{ \AA}^{-1}$ is characteristic of scattering from micropores. It is noted, however, that there is a considerable difference between the SAXS and SANS intensities in this region. That is, the SANS intensities are greater and extend to higher q values, and there is no significant coherent SAXS scattering for $q > 0.43 \text{ \AA}^{-1}$.

The observed difference between the SAXS and SANS data in the micropore scattering region derives primarily from the contrast factor between the pore void and the solid, $C_{s,p}$. In SAXS this is the electron density difference, $\Delta\rho_e$; while in SANS this is the neutron scattering contrast factor b_v . Most interpretations of SAXS data for porous materials assume that $C_{s,p}$ is determined exclusively by the electron density of the solid, and that it is a constant, such that it is factored out of the scattering integral. However, it is well known that enhanced adsorption of gases in microporous carbons is a consequence of overlapping potentials from the pore walls. Consequently, the finite electron density which exists within the carbon micropores effectively *reduces* the scattering contrast between the solid and the pore void. This can explain the apparent reduced scattering intensities exhibited in the micropore size range (i.e., at high q) in the SAXS data in Figure 3, in comparison to the SANS data. In addition, the electron density within the micropores is also a function of the pore size, and thus $C_{s,p}$ should also be a function of r , and, therefore, should be regarded as a variable, $\Delta\rho_e(r)$, which must be retained within the scattering integral in the case of SAXS. This is not the case for neutron scattering which is a consequence of interactions of neutrons with nuclei; and thus nothing within a pore void can contribute to b_v , irrespective of the pore size. Therefore, SAXS and SANS intensity data for microporous carbons should differ, and this difference may actually provide information about the electron density difference in micropores as a function of pore size, $\Delta\rho_e(r)$. Thus, the principal conclusion to be drawn from this comparison is that SAXS can be an unreliable technique for determining pore size distributions for microporous carbon materials, although the information it provides about the electronic structure of the micropores may be useful.

References

- [1] Thiyagarajan P, Epperson JE, Crawford RK, Carpenter JE, Klippert TE, Wozniak DG. J.Appl. Cryst. 1997;30:1.
- [2] Foster MD, Jensen, KF. SAXS investigation of model carbon pore structure. Carbon 1991;29(2):271-282.
- [3] Hall PJ, Antxustegi M, Calo, JM. Development of porosity in Pittsburgh#8. Energy&Fuels 1998;12:542-546.
- [4] Foster MD, Jensen KF. Interpreting scattering from random porous solids. J. Coll.Intf.Sci. 1990;135:132-146.
- [5] Vorres KS. Users handbook for the Argonne Premium Coal Sample Program, ANL/PCSP-93/1, 1993.

Acknowledgment

The IPNS is operated under Department of Energy contract number W-31-109-ENG-38.