POROSITY EVOLUTION *VIA* CONTRAST-MATCHING, SMALL ANGLE NEUTRON SCATTERING

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Introduction

A persistent problem in understanding the development of porosity in carbons and chars is the existence of closed porosity, which cannot be accessed from the exterior of particles using intrusive techniques. On the other hand, small angle scattering methods record data from both open and closed porosity, which cannot be distinguished. Additionally, such data may be complicated by interparticle scattering.

Recently, we have applied contrast-matching, small angle neutron scattering (SANS) to monitor porosity development in a glassy, phenolic resin char upon progressive activation [1]. It was shown that the activation process is due to opening up of "closed" porosity. Here we report on more recent results on a very different char.

Experimental

Analysis of porosity *via* contrast-matching involves the comparison of SANS data from two experiments on: (1) the dry, powdered sample; and (2) the same sample saturated with deuterated toluene. In the latter case, toluene fills all accessible porosity and interparticle voids. Deuterated toluene has about the same neutron scattering density as typical polycrystalline carbons (~5.6 10^{10} cm^{-2}) and, therefore, contrast-matches the carbon very closely. Consequently, the "open" porosity is "invisible" to neutrons, and the difference between the dry and contrast-matched samples is due to scattering in "open" pores, and interparticle scattering.

SANS data were obtained with the small angle diffractometer at the Intense Pulsed Neutron Source of the Argonne National Laboratory. Suprasil sample holders with a 2 mm path length were used. The data were corrected for scattering from the sample holder and for other instrumental backgrounds. Normalization for the sample thickness and transmission were made and the data were scaled to yield absolute calibrations.

Pittsburgh # 8 coal from the Argonne Premium Coal Sample Bank [2] was selected as the char precursor. Pittsburgh #8 coal is a coking coal which upon slow pyrolysis yields a very low surface area char with little microporosity, unlike phenolic resin char [1]. Coal samples were heated under nitrogen at 10 K/min to 1273K with a soak time of 1h. The resultant char was ground to between 60 and 100 Tyler mesh. For contrast-matching, samples were mixed with excess deuterated toluene and placed in an ultrasonic bath for 4h. Activation of the char was performed in air in a tube furnace at 673K

Results and Discussion

The N_2 adsorption isotherm and BET surface area (8 m^2/g) of the unactivated char were consistent with a nonporous material or a material with a pore system with significant amounts of meso- or macroporosity.

The SANS data for the unactivated char are presented in Figure 1. The "dry" curve shows no significant scattering for $q>0.15$ $Å^{-1}$, which suggests the absence of scatterers of less than ~40 Å, and the absence of well developed microporosity, consistent with the N_2 adsorption data. The monotonic increase in scattering with decreasing q indicates that the size of the largest scatterer cannot be resolved. This may be due to either interparticle scattering or scattering from a small number of large pores. A Guinier plot [3] (i.e., ln(I) *vs.* q^2) exhibits curvature over the entire q range, suggestive of a broad range of pore sizes.

From Figure 1 it can be seen that contrast-matching significantly reduces the scattered intensity at all q-values. The integral under the "dry" data is 2.19 and that under the contrast-matched curve is 0.10 (arbitrary units). Thus, scattering has been reduced by a factor of 22, and about 4.8% of the total scattering is due to closed porosity. This is compared to 59.9% for the unactivated phenolic resin char [1]. Figure 1 also shows that there is no significant scattering for $q>0.078$ $Å^{-1}$ for the contrast-matched sample, which suggests the absence of porosity less than ~75Å. It is probable, therefore, that scattering is due to a small number of large pores. The result is that the dry and difference curves are very similar.

Activation to 0.8% burn-off increases the N_2 surface area to 80 m^2/g, consistent with porosity development. The corresponding SANS data are similar to that for the unactivated char. The integral for the dry sample scattering data is 3.33, which decreases to 0.15 (arbitrary units) for the contrast-matched sample. Therefore, 4.8% of the total scattering is due to closed porosity, which is the same as for the unactivated char. Thus, the deuterated toluene can access all of the porosity developed upon activation. The SANS data from the 0% and 0.8% burn-off samples show that activation proceeds by the creation of new

porosity, rather than the opening of closed porosity as for the phenolic resin char [1].

Since the unactivated char has little or no porosity, the "difference" curve in Figure 1 is dominated by interparticle scattering effects. The scattering curve for this sample is close to Porod behavior [4] (i.e., $I \alpha h^{-3}$), which suggests that it is primarily due to the presence of relatively large scatterers. Since the increased surface area of the 0.8% burn-off char suggests porosity development, then the "difference" curve for these data must contain information about interparticle scattering as well as the additional porosity. Consequently, the difference between the two "difference" curves will be due to scattering from the additional porosity created upon activation. In this manner, the 0% burn-off "difference" curve can be used to correct the "difference" curves at other burn-offs for interparticle scattering effects.

SANS data at progressive levels of activation are presented in Figure 2. These are "difference" scattering curves corrected for interparticle scattering, as set forth above. Guinier analysis [3] shows a linear section with a radius of gyration, R_g = 16.3Å. Therefore, the early stages of activation appear to produce microporosity. The scattering curve for the 4.5% burn-off char in Figure 2 is also typical of a microporous network, and the corresponding Guinier plot is also linear with R_g = 13.5Å, indicating that additional microporosity is being produced. In contrast, the scattering curve for the the 13.5% burn-off char is typical of a pore system with a wide range of pore sizes. A Guinier plot confirms this by showing curvature over the entire q-range. A log-log plot is linear over the range $0.0058<q(Å^{-1})<0.054$, with a slope of -3.8. This deviates slightly from Porod behavior and is probably due to fractal roughening of the pore surfaces. The fractal dimension is 2.2, which agrees with other fractal investigations of activated carbon surfaces. Therefore, in the burn-off range 4.5%-13.5%, micropores appear to be opened to produce a pore system with a wide size range.

Conclusions

Contrast-matching SANS has been shown to be a very useful method for investigating porosity development in carbons and chars, both in terms of understanding the effects of closed porosity and the elimination of interparticle scattering effects. This technique was used to show that Pittsburgh #8 char has very little closed porosity, and that pore development during activation proceeds initially (<4.5% burn-off) by the creation of new pores and the development of significant microporosity. In later stages of activation (4.5%-13.5% burn-off), the tendency is to open these micropores, producing a pore system with a broad size distribution.

Acknowledgements

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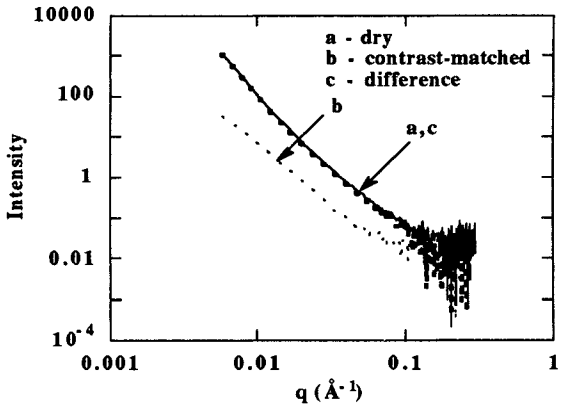

Figure 1. SANS data for unactivated Pittsburgh #8 coal char: (a) dry; (b) contrast-matched; and (c) difference, (a) - (b).

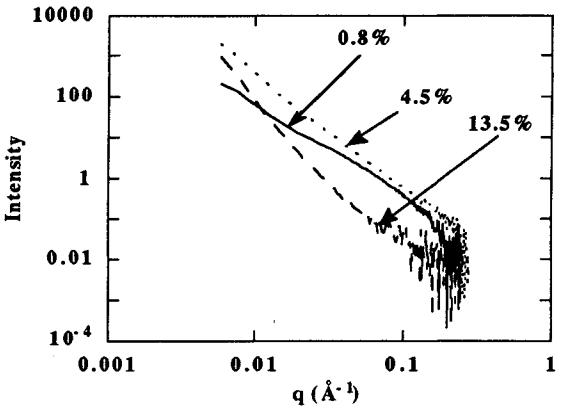

Figure 2. "Difference" SANS curves corrected for interparticle scattering for Pittsburgh #8 coal char at different levels of burn-off in air at 673K.