POSTER

CHARACTERIZATION OF THE MICROPOROUS STRUCTURE
OF SYNTHETIC ACTIVE CARBONS BY S.A.X.S

N. Cohaut[1], A. Bagreev[2] and J.M Guet[1]

1. C.R.M.D, rue de Chartres, B.P 6759, Université d'Orléans-CNRS, 45067 Orléans Cédex 2, France.
2. Institut for Sorption and Problems of Endoecology, Academy of Sciences of Ukraine, Kiev, Ukraine.

INTRODUCTION

Small Angle X-ray Scattering (S.A.X.S) is a non intrusive technique which completes with an efficient contribution the adsorptiometric methods to precise the evolution of carbon matter and the development of different porosities (1). The microtexture of synthetic active carbons from porous copolymers has been studied by S.A.X.S in order to measure its total porosity (opened and closed).

SAMPLES

Synthetic active carbons prepared from porous polymer precursors are used in various sorption processes (2) owing to high mechanical strength, well-developed porosity and appropriate physico-chemical properties.
Spherical granulated synthetic active carbons were prepared from porous styrene-divinylbenzene copolymer. Carbonization of copolymer was carried out in two stages: at 200°C in air with sulfuric acid and crosslinking agent, and at 700°C in inert atmosphere. The activation by water steam at 850°C and under 0.1 MPa pressure was carried out for different times in order to prepare carbons with a wide range of burn-off (8% to 71%). The samples of active carbons are heat treated at 950°C in inert atmosphere in order to stabilize their structure. The char preserves the spherical shape after carbonization and activation (diameter of particles 0.1 to 1mm). This processing is fully described in another abstract of this conference (3).

EXPERIMENTS

Adsorption experiments

Characterization of the synthetic active carbons was carried out by adsorption of N_2 at 77K and CO_2 at 273K and was described with more details in a paper of Bagreev et al (3). Micropore volume $V_0(cm^3/g)$ was determined from adsorption data using Dubinin-Radushkevich equation. The average width $d(nm)$ of slit-shaped micropores and geometric surface area $Sm(m^2/g)$ were calculated using the expression proposed by Stoeckli (4)
The true density of carbons was founded by means of helium picnometry method. The data obtained are summarized in table 1. Parameters of microporous structure of carbons with low weight-loss (2, 2A) were estimated from CO_2 isotherms and for others samples from N_2 isotherms.

S.A.X.S experiments.

Measurements were performed on ground samples with a 12kW Rigaku rotating anode X-Ray generator (5). All experiments were carried out under pinhole collimation conditions and the sample-to-detector distance was chosen to elucidate the porous texture in a size range from 5 to 120 Å. Experimental intensities are usually plotted versus $q=4\pi sin\theta/\lambda$ as the length of the scattering vector. S.A.X.S experiments are sensitive to the contrast of electonic density between two homogen phases such as voids in a solid carbonaceous matrix. At larger angles, S.A.X.S is also sensitive to the lamellar structure of carbonaceous matter, so that the intensity I(q) verify, for sufficient high q values the following expression:

$$I(q) = I_1(q) + I_2(q) = \frac{8\pi}{l_m}.\frac{1}{q^4} + \frac{\beta}{q^2}$$

$I_1(q)$ is due to an electronic contrast between pores and matter and $I_2(q)$ is due to distance fluctuations between carbon layers. After correction of the $I_2(q)$ component in the Porod plot $q^4.I(q)=f(q^2)$, the sample may be regarded as a two phase pores-dense matter system in which the mean length of chords in matter l_m is given by the Porod's law:

$$\lim_{q \to \infty} q^4.I_1(q) = \frac{8\pi}{l_m} = \frac{8\pi.P}{l_p.(1-P)} = \frac{2\pi}{S_v}$$

Where l_p is the mean lengh of chords in pores, S_v the surface area, defined as the intern surface by volume unit of matter and P the porosity, deduced from the expression:

$$P = \frac{1}{2.\pi^2} q^2.I_1(q).dq$$

RESULTS AND DISCUSSION

We have focused the S.A.X.S method on four actived samples (table 1). Samples 2 and 2A, both activated during 0.5h, were respectively studied before and after heat treatment at 950°C. Other samples were studied after heat treatment at 950°C and activation during 1h (3A) and 5h (5A). The scattering plots log I-log q are shown in figure 1. The comparison between curves 2 and 2A gives no evidence of a significant modification of the porous texture during heat treament at 950°C, while adsorptiometric methods show a decrease of pores mean size. Both records have a weak shoulder showing the presence of small pores, but as the Porod's law is not observed (Fig.2), we can conclude that the pores have too small dimensions to be separed from electronic heterogeneities due to matter disorder: the porosity can not be quantified. With higher activation time (3h, 5h), the Porod's law is verified (Fig.2) and deduced parameters show that after activation during 1h (3A), the porosity is

equal to 13.5%, this value is smaller than those reached after 5h (5A: 39.5%). The porosity's increase generates larger pores separated by thinner walls as shows the evolution of l_p and l_m parameters. In the assumption of spherical pores and isometric matter domains, the diameter of pores increases from $D=3.l_p/2=0.7nm$ for 3A sample to $D=1.4nm$ for 5A sample whereas the wall thickness decreases respectively from 4.3nm to 2.1nm. Consequently the surface area increases from 760 to $1360m^2/g$.

The mean size pores give by the two techniques are equivalent, even if assumptions on pores geometry are different. Both give evidence of an increase of the mean pores size with the activation time.

CONCLUSION

S.A.X.S technique was used on synthetic active carbon based on porous copolymers, to characterize the texture of porosity and the carbonaceous matter surrounding.

This method has shown that the size range of the developed porosity is very small. The increase of the mean pores size is obtained by the thinning of matter domains when the activation treatment increases from 1h to 5h. The S.A.X.S results, especially for the more activated sample 5A, are not so different from those given by adsorptiometry.

REFERENCES

1. J.M Guet, Coal Science and Technology, 15, Elsevier Science Publishers, 103, (1990).
2. V. Strelko, Ext. Abstr. Intern. Conf. on Carbon, Carbon'90, Paris, p 16, (1990).
3. A. Bagreev, V. Strelko, J. Dentzer and J. Lahaye, Ext. Abstr. 22nd Bien Conf. on Carbon, San Diego, (1995).
4. H. Stoeckli, L. Ballerini and S de Bernardini, Carbon, 27, 501, (1989).
5. N. Cohaut, Thesis, University of Orleans, France, (1993).

Table 1: S.A.X.S results compared with adsorptiometric data.

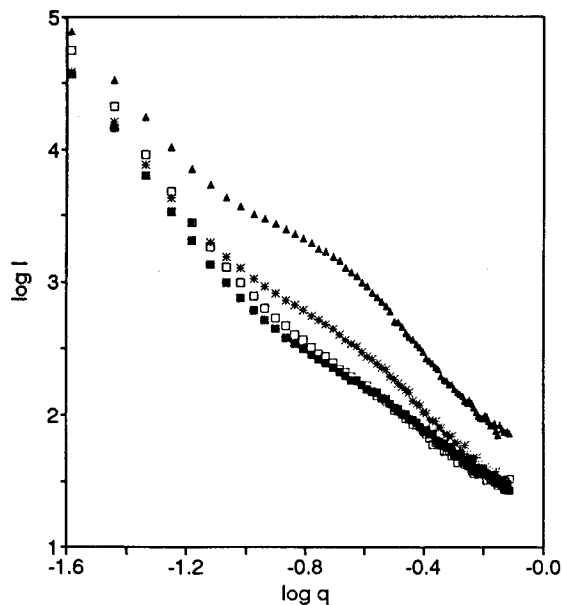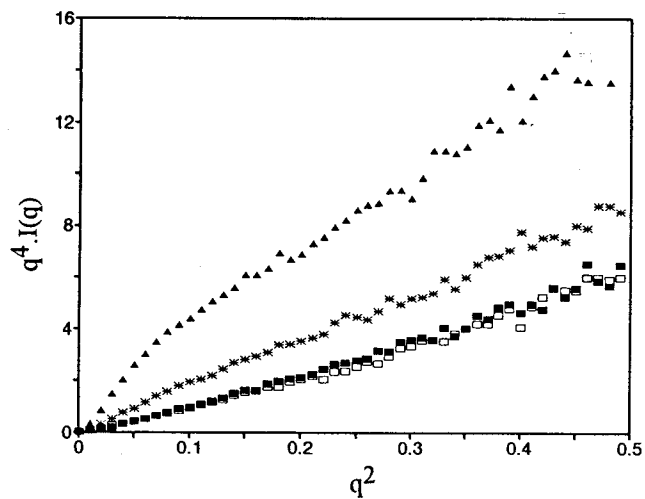| Samples	Activation time (h)	S.AX.S data					Adsorption data				
		Porosity %	l_m nm	l_n nm	S_v m^2/cm^3	S_v m^2/g	True density g/cm^3	Weight loss %	Vo cm^3/g	d nm	Sm m^2/g
2	0.5	-	-	-	-	-	-	8	0.13	0.95	273
2A	0.5	-	-	-	-	-	1.76	13	0.21	0.54	790
3A	1	13.5	2.9	0.45	1400	760	1.85	27	0.28	0.72	785
5A	5	39.5	1.4	0.9	2920	1360	2.15	75	0.55	1.29	861

Figure 1: S.A.X.S: log I-log q plot:
■: 2, □: 2A, ✳:3A, Δ:5A

Figure 2: S.A.X.S Porod's plot:
■: 2, □: 2A, ✳:3A, Δ:5A