STUDY OF POROSITY OF ACTIVATED MONOLITHES BY SAXS AND ADSORPTION TECHNIQUES

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Introduction

The use of active coals as catalyst supports is a good choice because their high surface area allows increasing the interactions between catalysts and species to be treated. However they present some disadvantages as the presence of ashes (or other impurities), their microporosity is not always accessible and their mechanical properties are generally rather low. For those reasons, we have elaborated a monolithic activated carbon obtained after compression of an expanded graphite which was assumed to realize a good compromise between mechanical properties and pore accessibility. Furthermore, this monolith is ash free.

Experimental

Expanded graphite has been compressed in one direction in a block (sample CG). After impregnation with furfurylic alcohol which is then polymerised, this block is heat treated under nitrogen at 550°C in order to eliminate volatile matter. After that, we get a graphite based monolith finely recovered of a thin layer of semi-coke(sample ICG). A steam activation at 800°C of this monolith, with a burn-off of 40%, permits to generate porosity within this thin layer(sample AICG).

The porosity evolution of this monolith has been studied during all these steps by different techniques: C_6H_6 and CO_2 adsorption isotherms, He pycnometry and Hg porosimetry, as well as a non intrusive technique: the Small Angle X-ray Scattering (SAXS) method which permits to have access to the global (open and closed) porosity.

Results and Discussion:

POROSIMETRY

Porosimetry data, performed on monoliths at different stages of treatment, are gathered on table 1. The starting expanded graphite has a bulk density, as measured with Helium, of 0.7 g/cm^3. After compaction, the comparison of bulk and skeletal densities permits us to see that the sample stays highly porous: 90%.

After impregnation, porosity decreases, showing that at this stage of treatment, 30% of this porosity has been filled by resin, which seals the entry of pores and induces artificially a fall in the measurement of porous volume, pore surface area and average thickness of pores.

During the activation, if we suppose that expanded graphite is quite not affected , the comparison of values of porous volume before and after activation (measurements with Hg) shows that the resin develops by activation a porosity of around 10% in the mesoporosity accessible to Hg.

SAXS

Small Angle X-Ray Scattering (SAXS) is a non intrusive technique, well adapted to investigate the global porosity of carbons [1-3].The figures 1 and 2 show log-log plots of the scattered intensity I(q) of monoliths in different stages of preparation: this intensity is expressed versus the Bragg's distance (d=2ð/q).

These curves show the heterogeneity of the elaborated material in a scale going from 100 Å to 5Å, covering the range of micropores and partially the range of mesopores, that permits us to study the porosity of the activated resin: after impregnation, the X-ray scattering contribution of the resin can be easily separated from those of the substrate (sample CG in the Fig.1), taking into account the distinct scales of their porosities. The polymeric structure gives a constant background at a scale inferior to 26Å ($q<0,12Å^{-1}$). Beyond it is the expanded graphite structure which appears on the curve (Fig. 2).

Conclusions

This study shows that during the impregnation (sample ICG),one the third of porosity fills of resin, and SAXS curves are sensitive to the electronic contrast of density of this resin.

After activation, the sample AICG developed approximately 10% of additional porosity in the resin. The SAXS curves

show then a contrast of density micropores/matter at a scale lower than 15Å.

References

1.Guet J.M. Coal Science and Technology, vol.15, Elsevier, 1990: 103-113.

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3. Cohaut N. et al Carbon 2000 ;38 :1391-1400.

Table 1: Results from Hg Porosimetry and He Pycnometry:

Sample	D_b	D_s	V	A	e_{50}	P
CG	0.14	1.3	6	110	0.5	90
ICG	0.56	1.52	1.1	48	0.3	63
AICG	0.52	2	1.1	54	0.25	74

D_b: bulk density (g/cm^3)
D_s: skeleton density (g/cm^3)
V: porous volume (cm^3)
A : pore surface area (m^2/g)
e_{50}: median thickness (□m)
P: volume fraction of opened pores (%)

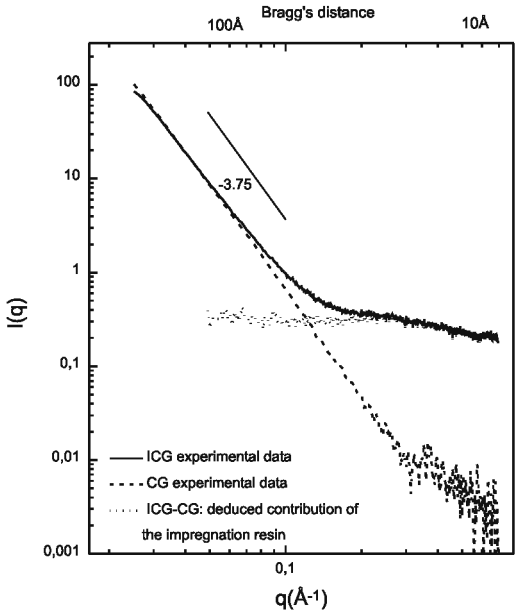

Fig.1: Scattering curve of impregnated monolithe

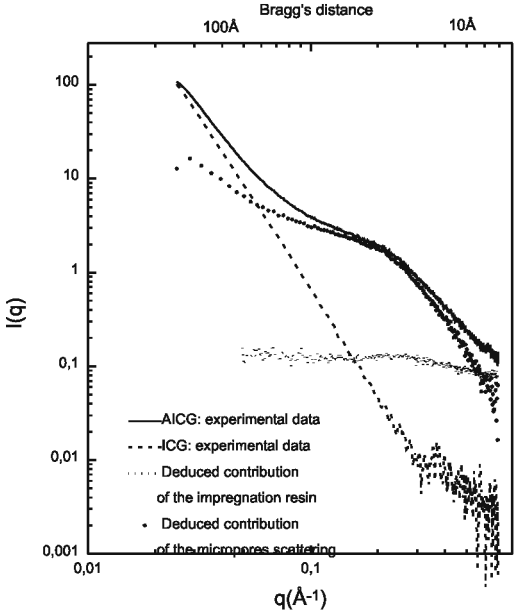

Fig.2: Scattering curve of activated monolithe