

MICROPOROUS STRUCTURE AND ACTIVE SURFACE AREA OF SYNTHETIC ACTIVE CARBONS

A.Bagreev, V.Strelko, J.Dentzer* and J.Lahaye*

Institute for Sorption and Problems of Endoecology,
National Academy of Sciences of Ukraine, 32/34 Av. Palladin, 252680 Kiev-142, Ukraine
*Centre de Recherches sur la Physico-Chimie des Surfaces Solides, 24 Av. Kennedy, 68200 Mulhouse, France

INTRODUCTION

Synthetic active carbons (AC's) prepared from porous copolymers and spherical granulated resins are used as efficient sorbents for the cleaning of gases and solutions due to their unique chemical and physical properties [1,2].

The peculiarity of synthetic AC's is that the formation of the meso- and macroporosity is possible at the stage of preparation of the precursors - porous copolymers and resins [2]. Microporosity in synthetic AC's are formed during the process of activation at higher temperature by carbon dioxide, water steam or oxygen.

The active surface area (ASA) [3] has a great importance for the understanding the kinetics of gasification and the development of porous structure of carbon materials during activation [4,5].

In the present paper the evolution of the microporous structure and ASA of synthetic AC's are compared.

EXPERIMENTAL

A spherical granulated synthetic AC (SCS-type) prepared from porous styrene-divinylbenzene copolymer by means of carbonization at 973 K followed by activation with water steam at 1123 K has been chosen for investigation.

The porous structure of these carbons was investigated by CO₂ (273 K) and N₂ (77 K) adsorption. The adsorption data of CO₂ and N₂ on the synthetic AC SCS were analyzed according to the Dubinin-Radushkevich (DR) equation:

$$V = V_0 \exp(-(A/\beta E_0)^2), \quad (1)$$

where $A = -RT \ln(P/P_0)$ is the differential free energy of adsorption; V is the volume of the adsorbate condensed in the micropores at the temperature T and the relative pressure P/P_0 ; V_0 is the total volume of micropores

accessible to the adsorbate; β is the affinity factor; E_0 is the characteristic energy of adsorption.

The size of micropores (d) was calculated from the DR plots using the relation between (E_0) and the average width of slit-shaped micropores, proposed by H.F.Stoeckli [6]:

$$d = 30/E_0 + 5705/E_0^3 + 0.028E_0 - 1.49. \quad (2)$$

The surface area of the micropores (S_m) was determined using equation

$$S_m = 2 V_0/d. \quad (3)$$

The ASA was measured according to the oxygen chemisorption method developed by N.R.Laine et. al.[3] with using the temperature-programmed desorption (TPD) technique [7]. The ASA values were calculated from the TPD curves for CO and CO₂.

The ASA were also determined by the flow microcalorimetry method developed by A.J.Groszek [8]. This method is founded on the determination of the polar sites area of carbons by means of measuring of preferential heat of adsorption of n-butanol on carbon samples immersed in n-heptane.

RESULTS AND DISCUSSION

Using porous styrene-divinylbenzene copolymer as precursor enables to produce spherical microporous active carbons with high mechanical strength and low ash content.

The samples of synthetic carbon with low burn-off are characterized (Tabl.1) by the presence of a significant volume of micropores (ca 0.50 nm). The pore volume and micropore size obtained by N₂ adsorption are higher than that for the CO₂ adsorption for the samples with middle and high burn-off. Probably, this two adsorbates are

measuring the different type of microporosity in highly activated carbons: N₂ filled the whole micropore volume whereas CO₂ would only measure the narrow micropores.

A good agreement is obtained for the ASA determined by oxygen chemisorption and the polar sites area obtained by the microcalorimetry method (Tabl.2). The discrepancy for SCS-1 is attributed to a molecular sieving effect for n-butanol adsorption (the average size of micropores for SCS-1 is equal to the diameter of n-butanol molecule (0.5 nm)). The surface polarity indices (SPI) calculated by dividing the heat of n-butanol adsorption by the surface area of micropores for carbons with various burn-off are presented in Table 2. The SPI, which characterizes the surface polarity of AC's by microcalorimetry method in whole, is increasing with the oxidation treatments, which is in agreement with A.J. Groszek data [8].

The determination of active surface area combined with characterisation of micropore structure enables to follow the changes occurring during activation of SCS carbon. The micropore volume, average micropore size and ASA increases significantly by activation, while the total surface area passes through a maximum. The ratio of ASA to micropore surface area remains almost constant (0.04)

Table 1. Pore structure characteristics of synthetic active carbons SCS.

Sample	Burn-off, %	V ₀ , cm ³ /g	E ₀ , kJ/mol	d, nm	S _m , m ² /g
SCS-1	3	0.119	33.6	0.50	441
SCS-2	13	0.212	31.0	0.54	790
SCS-3	27	0.271	28.9	0.60	911
SCS-4	60	0.364	26.5	0.69	1062
SCS-4(*)	60	0.460	22.0	1.02	901
SCS-5	75	0.371	25.1	0.77	964
SCS-5(*)	75	0.554	20.0	1.29	861

* - calculated from nitrogen adsorption isotherm.

during activation and its value is similar to those obtained for other activated carbons prepared from polymers [5,7]. The low value ASA/S_m indicates that the walls of the micropores of synthetic AC SCS consist mainly of basal planes and that is in agreement with a previous study of P.Ehrburger [5].

REFERENCES

1. V.V.Strelko, Proc. Carbon-90, France, Paris (1991).
2. N.T.Kartel, A.M.Puziy, V.V.Strelko, Characterization of Porous Solids-II, Elsevier, Amsterdam (1991).
3. N.R.Laine, F.J.Vastola, P.L.Walker Jr., J.Phys. Chem., 67 2030 (1963).
4. Fundamental Issues in Control of Gasification Reaction (Edited by J.Lahaye and P.Ehrburger). NATO ASI Series, vol.192 (1991).
5. P.Ehrburger, N.Pusset, P.Dziedzic, Carbon, 30 1105 (1992).
6. H.F.Stoeckli, L.Ballerini and S.De Bernardini, Carbon, 27 501 (1989).
7. P.Causton and B.McEnaney, Fuel, 64 1447 (1985).
8. A.J.Groszek, Carbon, 25 717 (1987)

Table 2. Variation of ASA and polar sites area of SCS carbons during activation process.

Burn-off, %	ASA, m ² /g	ASA/S _m	CO/CO ₂	Polar sites area, m ² /g	SPIx10 ⁻³ , J/m ²
3	30.3	0.069	8.0	12.2	4.1
13	29.9	0.039	7.3	25.0	4.7
27	36.5	0.040	8.9	31.2	5.1
60	41.0	0.039	10.4	39.3	5.5
75	43.3	0.045	12.2	46.6	7.2