

MODELING OF POROSITY DEVELOPMENT IN ACTIVE CARBONS

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Introduction

Porous structure of carbons is one of the main factors determining their industrial application. That is why the methods, which permit to describe or to predict the porosity formation in activation process, are very important. The objective of this study is to demonstrate the possibility for the prediction of pore structure evolution in carbon activation process. The Random Pore Model (RPM) and Pore Population Balance (PPB) equation are used [1-3].

Experimental

Active carbons (AC) were prepared by steam and carbon dioxide activation in a quartz tube reactor at 1073, 1123 and 1173K and pressure 0.1 MPa. Porous styrene-divinylbenzene copolymer was used as a precursor for carbon preparation. Carbons with a burn-off range 0-70 % were obtained [4]. The porous structure of carbons was studied by CO₂ (273K) and N₂ (77K) adsorption. Volume of micropores, their surface area and pore size distribution are evaluated using D-S equation.

Modeling

The model of spherical shape pores which are randomly distributed in a carbon matrix and overlapped is applied (Random Pore Model) [1-3]. Suppose that $f(r, t)$ is the pore size distribution (PSD) function and $f(r, t)dr$ is the number of pores per unit volume of carbon having a radius between r and $r+dr$ at the time t . During the activation the pore size changes because carbon from pore walls reacts with oxidizing agent. Number of pores increases due to nucleation of new ones. Then the evolution of PSD function obeys the PPB equation:

$$\partial f(r, t) / \partial t + W \partial f(r, t) / \partial r + D \partial^2 f(r, t) / \partial r^2 = I(t) \delta(r - r_c) \quad (1)$$

$$\text{with initial conditions} \quad f(r, 0) = f_0(r), \quad (2)$$

$$\text{and boundary conditions} \quad f(\infty, t) = 0, \quad (3)$$

$$\{W f(r, t) + D \partial f(r, t) / \partial r\} \Big|_{r=r_c} = I(t), \quad (4)$$

where W is the rate of the single pore growth; D is the coefficient of rate fluctuation ("effective diffusion"); $I(t)$ is

the rate of new pores nucleation per unit volume; $\delta(r - r_c)$ is the delta Dirac function; r_c is the size of pore nucleus.

All effective parameters of non-overlapping pore structure, such as an average pore size ($\langle r \rangle$), total pore length (L_E), specific surface area (S_E), porosity ($V_E(t)$) can be calculated by integration of PSD function obtained from the solution of eq 1. In the process of activation the size of existing pores is increased, new ones are nucleated, and then started to overlap. This effect leads to decreasing of actual porosity (ε), surface area (S), length of pores (L). According to RPM relationship between effective and actual parameters is [1]:

$$\varepsilon = 1 - \exp(-V_E), \quad S = S_E(1 - \varepsilon), \quad L = L_E(1 - \varepsilon) \quad (5)$$

The effective PSD ($f(r, t)$) and PSD of slit-shaped pores ($v(x, t)$) usually used in adsorption are linked by equation:

$$v(x, t) = f(r, t) (1 - \varepsilon) k_f r^3 / d, \quad (6)$$

where x is the pore width, d is apparent density of AC, k_f is the coefficient of pore form. If the size of AC particles slightly decreases by activation, the burn-off (X) and apparent density of AC with a low ash content are connected with porosity by:

$$X = (\varepsilon - \varepsilon_0) / (1 - \varepsilon_0), \quad (7)$$

$$d = d_0 (1 - \varepsilon) / (1 - \varepsilon_0), \quad (8)$$

where ε_0 , d_0 are the initial porosity and density.

Results and Discussions

The micropore size distributions and parameters of D-S equation for carbons with different burn-off are shown in Figure 1 and Table 1. These data clearly demonstrate that D-S equation can describe the microporosity development in AC. Hence these data can be used for the examination of RPM.

Biporous (micro- and mesoporous) model of AC is used. Three general types of RPM were studied. For the first it was assumed that new pores were not initiated ($I=0$) and "diffusion" is negligible ($D=0$). For this case the solution of eq 1 is very simple: $f(r, t) = f_0(r - Wt)$, which means that PSD function moves initial distribution parallel with the rate W , and an average pore width ($\langle x \rangle$) increases linearly with time of activation (curve 1 Fig. 2a).

Table 1. Parameters of pore structure of carbons calculated from D-S equation. Steam activation at 1123 K.

Burn-off, %	V_{mic} , cm^3/g	$\langle x \rangle$, nm	σ , nm	S_{mic} , m^2/g
0	0.19	0.66	0.14	690
6	0.27	0.72	0.19	805
20	0.36	0.80	0.22	955
50	0.58	1.10	0.30	1140
70	0.69	1.20	0.33	1210

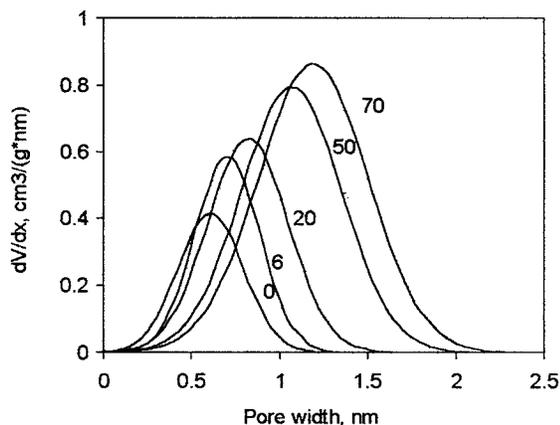


Figure 1. Micropore size distributions for carbons with different burn-off.

Curves 2-4 in Fig.2 demonstrate the behavior of the model when ($D=0$) and nucleation rate corresponds to the heterogeneous nucleation law:

$$I(t) = k_1 I_0 (1 - \varepsilon) \exp(-k_2 t), \quad (10)$$

where k_1 , k_2 are the nucleation rate constants, I_0 is the number of pore "germs" per unit volume of AC at $t=0$. The digital method solution of eq 1 is applicable for PSD. The dependencies for integral parameters of porous structure vs. time can be easily received using method of PSD moments [3]. The average pore width passes through the minimum if nucleation occur, while total surface area passes through maximum. Such dependencies are often observed for CO_2 activation. The dependencies for burn-off vs. time have "S"-shape for the carbons with small initial porosity.

In the case of significant heterogeneity of carbon surface and a big fluctuation in the rate of pore growth ($D/W^2 \Delta t > 1$) the behavior of PSD is complex. In general the effective PSD is transformed according to the "chromatographic law for pulse injection", while this transformation for $v(x,t)$ is more complex. The successful fitting of calculated and experimental PSD may be achieved by varying the parameters W and D .

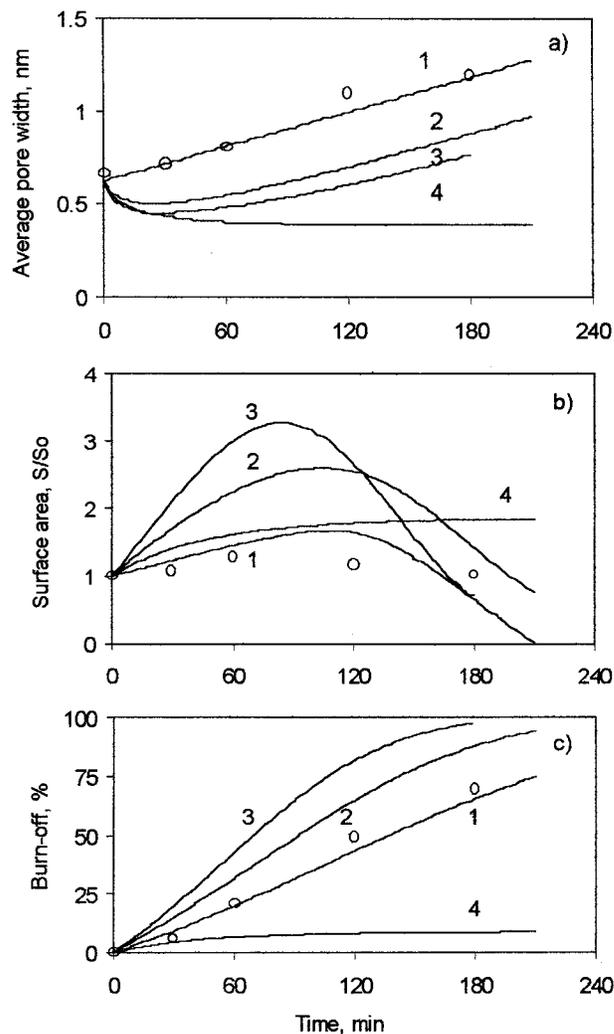


Figure 2. Evolution of average pore size (a), surface area per unit volume (b) and burn-off (c) of carbons. Points – experiment. Curves: 1- pore growth without nucleation; 2,3-nucleation and pore growth; 4- nucleation only.

Acknowledgments

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