DEVELOPMENT OF MICROPOROSITY IN SYNTHETIC ACTIVE CARBONS BY ACTIVATION OF STEAM AND CARBON DIOXIDE

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Introduction

Selection of the activating agent is one of the main factors for the production of microporous activated carbons (AC's). It was found for AC's prepared from various precursors [1-3] that activation by carbon dioxide creates the new microporosity whereas steam develops the existing microporosity.

Early [4] the steam gasification of nitrogen containing carbon prepared from porous vinylpyridine resin was investigated. The aim of this study is to compare the development of microporosity and micropore size distribution of synthetic active carbons prepared by steam and carbon dioxide activation.

Experimental

Two series of synthetic AC's were prepared using a porous vinylpyridine-divinylbenzene copolymer as a precursor. In both cases carbonization of initial copolymer was carried out in two stages: in air at 623 K and then in argon at 1223 K. A carbonized polymer (C) has been activated by steam at 1073K and 1123K and pressure 0.1 MPa. By varying time of steam activation, carbons of series (W) with a burn-off range 6-72 % were obtained [4]. These carbons are compared with series (D) obtained by gasification of the same char (C) in pure carbon dioxide at 1123 K and 1173 K. This series covers the burn-off range 7-66%. The conversion is included in the name of the sample: W21 corresponds to the carbon activated by H_2O to 21% of burn-off.

The porous structure of synthetic AC's was studied by CO_2 (273 K) and N_2 (77 K) adsorption. Micropore volume (V_0) was determined from the adsorption isotherms of CO_2 and N_2 according to D-R equation. The size of micropores (L) was calculated from D-R plots using the relation between the characteristic energy of adsorption (E_0) and average width of slit-shaped micropores, proposed by H.F.Stoeckli [5]:

$$L = 30/E_0 + 5705/E_0{}^3 + 0.028E_0 - 1.49$$

The number of micropores was determined by Dubinin method [6] using the model of microporous zones. The Pore Size Distribution (PSD) in AC's was evaluated from isotherms of nitrogen adsorption according to Jaroniec-Choma (J-C) equation [7].

Results and Discussion

Activation of initial char by H_2O or CO_2 leads to significant weight loss. The rate of H_2O activation higher than one for CO_2, e.g. at 1123 K the ratio between H_2O and CO_2 rates is near 5.

In order to compare the development of microporosity in synthetic carbons during activation by various gases it is convenient to present the data (Fig.1) for volume, average size and number of micropores as a function of burn-off (X). The temperature of activation has not an effect on the course of plots and experimental points for different temperatures form a group around common curves corresponding to activating agents.

Micropore volume calculated per current carbon mass increases linearly with burn-off for both oxidizing gases (Fig. 1a). The development of microporosity during CO_2 activation is more significant then for steam activation. For X=60% the micropore volume reaches the value 0.6 cm³/g for H_2O and 0.75 cm³/g for CO_2 activation.

The average size of micropores increases with burn-off, moreover in series W the pore size is higher than in series D for all range of X (Fig.1b). For small burn-off the plots of L vs. X is different in series W and D. For steam activation L increases from 0.51 nm to 0.79 nm (W21), whereas for CO_2 activation L increases only to 0.56 nm (D19), although V_0 in sample D19 is the same as in W21 (Fig.1a).

Figure 1c shows the variation of the number of micropores during activation process (N_0 is the number of micropores in sample C). In series W it is observed the significant (70% for W21) reduction the number of micropores for small burn-off, whereas for activation by CO_2 this reduction is only 10-20 % (D19 and D17). At high burn-off N decreases strongly and becomes approximately equal for two series of AC's.
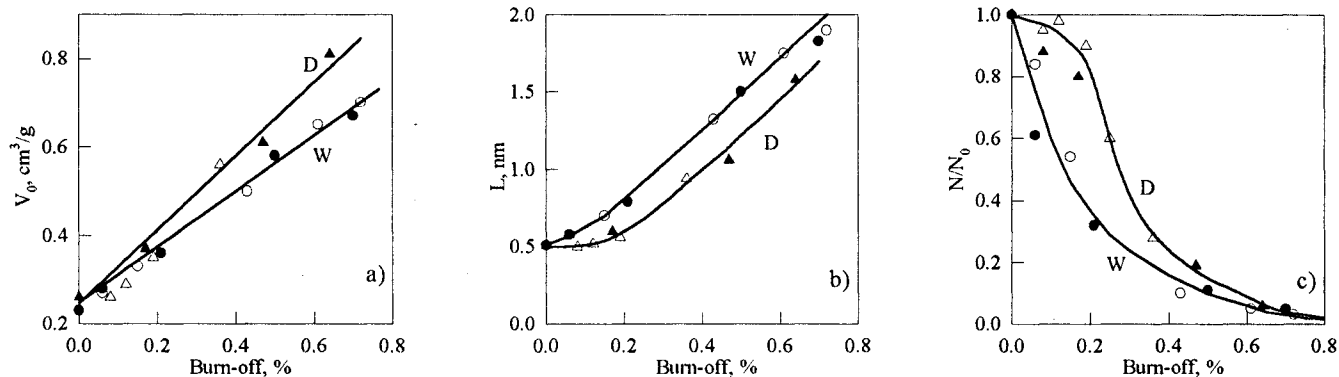
Figure 1. Evolution of volume (a), average size (b) and number (c) of micropores in synthetic AC's as a function of burn-off. Series W - for steam and D - for carbon dioxide activation. Temperature:○-1073 K;●, △-1123 K; ▲-1173 K.

The pore size distributions were calculated according to J-C equation for series W and D. The AC's under investigation have nonuniform microporous structure, moreover the degree of heterogeneity increases with burn-off. In series D the maximums on the plots of PSD are shifted to smaller sizes with comparison to series W for all burn-off range. On Fig.2 the PSD's for samples W50 and D46 having approximately the same micropore volume are shown.
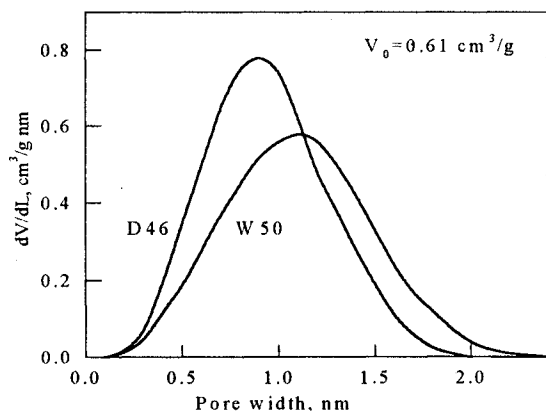

Figure 2. Pore size distribution calculated by J-C equation for carbons activated by steam (W50) and carbon dioxide (D46).

The obtained data on evolution of microporosity in synthetic AC's can be explained by following means. Initial char has significant micropore volume (0.23 cm^3/g) with pore size 0.5 nm and sufficiently high (34.5m^2/g) active surface area [4]. Under interaction with activating gases the gasification initiates on the active sites of micropore walls. For H_2O the reaction occurs in the existing micropores that leads to increasing their average size and volume. The number of micropores decreases owing to coalescence a few pores into one at small burn-off and transition of large micropores into

mesopores at high burn-off. For CO_2 the activation occurs by some another way: together with the growth of existing micropores takes place the processes of the creation of a new more small pores, their growth and coalescence. The reasons of the creation of new pores for CO_2 activation may be caused by the formation and decomposition of oxygen surface groups [1,3].

The balance between the processes of creation, disappearance and growth of micropores during gasification will be determine the evolution of PSD and the number of micropores, their average size, surface and volume accordingly.

References

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