

CONVERTING LONG-FLAME COAL INTO NANOPOROUS CARBON MATERIAL DURING CARBONISATION WITH POTASSIUM HYDROXIDE

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The article is devoted to the study of changes in the supramolecular and porous structure of long-flame coal during its transformation into a nanoporous material in the process of carbonisation with potassium hydroxide at a low KOH/coal ratio $R_{\text{KOH}} = 1.0$ g/g.

Samples of carbonaceous materials (CM) were prepared in argon by heating (4 deg/min) to a given temperature t (in the range of 350-825 °C), isothermal holding for 1 h, cooling, alkali washing, and drying. The samples are denoted as CM(t). The yield and elemental composition of CM were determined. The supramolecular structure of the CM was studied by XRD (Bruker D8). The interlayer distance in crystallites d_{002} , height L_c , average diameter L_a and crystallite volume V_c , intensity I_{002} of the reflex (002) were determined. Based on the low-temperature (77 K) nitrogen adsorption-desorption isotherms by the 2D-NLDFT-NS method, the integral and differential dependences of the specific surface area of S_{DFT} (m^2/g) and the pore volume V (cm^3/g) on the average pore diameter (D , nm) were calculated (SAIEUS software). From these, the volumes of ultramicropores (V_{umi}), supermicropores (V_{smi}), and micropores (V_{mi}) were calculated. The total pore volume was calculated from the amount of nitrogen adsorbed at a relative pressure of $p/p_0 \sim 1.0$. Similarly, the specific surfaces of ultramicropores (S_{umi}), supermicropores (S_{smi}), and micropores (S_{mi}) were determined.

It has been established that under conditions of alkaline carbonisation with KOH, long-flame coal is converted into CM with a yield of 45.3-70.2 %, a specific surface area of up to 1530 m^2/g and a total volume of adsorbing pores of up to 1.091 cm^3/g . With increasing temperature, the carbon content of CM decreases from 77.2 % to 71.3 % (at 500 °C), and then increases to 85.9 % (at 825 °C). The oxygen content increases to a maximum at 500 °C due to reactions in which KOH is a donor of O-atoms, and then decreases due to thermal destruction of functional groups and condensation reactions that increase the size of polyarenes of the secondary framework of the CM and form single $C_{\text{ar}}-C_{\text{ar}}$ bonds between them. The main changes in the supramolecular structure occur above 400 °C and lead to an increase in d_{002} from 0.407 nm to 0.446 nm, a decrease in L_c from 0.872 nm to 0.699 nm, and an increase in the size of polyarenes L_a from 1.46 nm to 3.30 nm. Judging by the ~3-fold decrease in the I_{002} intensity, the crystallite content decreases significantly with increasing temperature, and the degree of amorphousness of the spatial framework of the CM increases. It was found that the thermally initiated reactions of coal with KOH form mainly pores with $D \leq 5$ nm. With increasing temperature, the total pore volume and micropore volume increase monotonically. The values of V_{umi} and V_{smi} increase up to 600 °C, and at 600-825 °C, the volume of V_{umi} decreases, since ultramicropores ($D \leq 0.7$ nm) are transformed into supermicropores ($D = 0.7-2.0$ nm) due to the burnout of pore walls. The proportion of ultramicropore volume is maximum (23.9 %) in the sample CM(600). The proportion of the specific surface area of ultramicropores is maximum (56.3 %) in CM(500). The proportion of the micropore surface is dominant (92.6-97.0 %) in the CM obtained at $t \geq 450$ °C. The distributions of pore volume and specific surface area are characterised by maxima corresponding to subnanopores with $D \leq 1$ nm, supermicropores and mesopores with $D = 3-5$ nm. For the CM samples obtained at 450-750 °C, there are no supermicropore maxima, but their formation occurs. It was determined that the most microporous CM are formed at 785-825 °C and are characterised by a specific surface area of 1514-1522 m^2/g , a pore volume of 1.047-1.091 cm^3/g , and a micropore surface area of 1415-1443 m^2/g , which is not less than 93 % of the total surface.

Keywords: long-flame coal, alkaline treatment, carbonisation, carbonaceous material, supramolecular structure, porosity.

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