NANOPOROSITY FORMATION OF BROWN COAL ADSORBENTS DURING HEAT-SHOCK ALKALI ACTIVATION

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Alkaline activation is a well-known method for the porous structure development of adsorbents from any kind of carbonaceous solids: polymers, biomass, coke, pitch, graphene, different rank coals. A significant development of the specific surface area ($S \geq 2000$ m^2/g) is observed when using large alkali/coal ratios ($R \geq 2$ g/g) under ordinary activation conditions, comprising two stages: 1) thermoprogrammed heating (4–10 deg/min) to 800 °C and 2) isothermal exposure (≥1 h). Carrying out stage 1 as a heat shock (HS) - the rapid introducing of samples into a reactor zone pre-heated up to 800 °C makes it possible to develop a surface up to S = 1500–2000 m^2/g at low ratios R = 0.5–1.0 g/g.

The aim of this work is to study the nanoporous structure of brown coal adsorbents prepared by alkaline activation varying temperature of heat shock t_{HS}.

A t_{HS} increase in the range from 400 to 800 °C causes a decrease in the activated solid yield from 67 % to 25 % and an increase in the specific surface to S~2000 m^2/g (Table). The main development of the surface occurs due to formation of pores with a diameter ≤5 nm and only at t_{HS} =400 °C the pores with D≤4 nm are not formed. The micropores surface S_{mi} (D≤2 nm) and subnanopores surface S_{1nm} (D≤1 nm) develops predominantly at $t_{HS} \geq 400$ °C. Their portions (S_{mi} /S and S_{1nm} /S) sharply increase to 600 °C and then (from 600 °C to 800 °C) change slightly while the specific surface of these pores monotonically increases with increasing heat shock temperature.

Table. Yields and pore structure characteristics of brown coal adsorbents (R = 1.0 g/g)

Parameter	Heat shock temperature t_{HS}, °C						
	400	500	600	650	700	750	800
Yield, %	67	51	46	42	35	29	25
S, m^2/g	14.7	317	515	664	993	1481	1947
S_{mi}, m^2/g	0	252	478	601	930	1380	1869
S_{1nm}, m^2/g	0	166	444	581	917	1365	1840
S_{mi} / S_Σ	0	0.795	0.928	0.905	0.937	0.932	0.960
S_{1nm} / S_Σ	0	0.524	0.862	0.875	0.923	0.922	0.945
dS_1, m^2/g·nm	0	538	1260	1850	2930	4230	7340
dS_2, m^2/g·nm	0	169	49	38	21.6	9.2	69
dS_3, m^2/g·nm	2.3	13.4	18.8	30.9	34.3	63.1	45.8
V_Σ, cm^3/g	0.124	0.355	0.322	0.471	0.568	0.867	0.892
V_{mi}, cm^3/g	0	0.051	0.142	0.180	0.283	0.426	0.526
V_{1nm}, cm^3/g	0	0.126	0.169	0.197	0.293	0.433	0.547

The specific surface distribution, defined as (dS/dD)-D relationship, is characterized by maxima dS_1, dS_2, dS_3 in the pore diameter ranges D≤1 nm, micropores with D = 1–2 nm, mesopores with D>2 nm, respectively. The dS_1 maximum value increases with temperature according to the Arrhenius equation ($r^2 = 0.983$). The effective activation energy (E_{S1}) for a process of the subnanopores surface area increment E_{S1} = 56.7 kJ/mol, where mole is the quantity of surface atoms that must be removed to form a 1 m^2 specific surface. Pore size distribution as dV/dD-D relationship changes with t_{HS} in the same manner; the value of E_{V1} = 56.7 kJ/mol (r^2 = 0,989) is equal to the E_{S1} value.

Thus, the heat shock is a powerful method to develop the nanoporous structure of the brown coal adsorbent during alkaline activation.