

CARBONIZATION OF COALS RESTRUCTURIZED VIA INTERCALATION - LIKE REACTIONS

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Introduction

Preliminary chemical treatment of coals changes their properties and behaviour under heating, in particular, enhances the surface area development during the chemical activation [1-3]. The aim of the present work is to investigate the effect of structural reorganization of coals on their carbonization in an inert atmosphere and in the presence of potassium hydroxide as an activating agent in preparation of carbon adsorbents. Special attention is focused on the chemical modifications of coals obtained by the graphite intercalation- like reactions using oxidative systems which generate nitronium cation, NO_2^+ , and acid anions, A^- [4]. Such systems are assumed to promote the conversion of coal arenes into their cationic species by way of: (i) electron abstraction and its transfer to the external space with gaseous NO_2 , (ii) arenonium ion formation owing to the attack of powerful nucleophile on aryl carbon atom [5]. The positive charges formed are neutralized by anions inserted in the framework of coal. The whole complex of the reactions causes an essential and irreversible restructurization of the coal lattice [6].

Experimental

Coking coal from Donetsk coal basin (C 88,6, H 4,8, S 1,5, VM 20,7 daf %, A^d 4,8 %, size fraction 0,05-0,20 mm) was dried and then oxidized at room temperature. The oxidative systems selected for this study were NO_2BF_4 in acetonitrile, fuming HNO_3 and its mixtures with H_2SO_4 , acetic or trifluoroacetic anhydrides. Concentration ratio oxidant (NO_2^+)/coal, was varied from 1 to 100 mol/kg, experimental procedures used were described in detail elsewhere [3, 4, 6].

Results and Discussion

Coal restructurization is caused by electrophilic substitution reactions, fixation of molecules and ions within the organic lattice and covalent bonding of inserted oxygen atoms, as determined by diffuse reflectance infrared spectrometry (DRIFT). DRIFT-spectra indicate the presence of nitro groups (1535 and 1344 cm^{-1}), ethereal C-O bonds (1282 - 1278 cm^{-1}), conjugated keto groups (1685 - 1682 cm^{-1}) whereas conjugated H atoms (811 cm^{-1}) disappear completely. Reorganized coal framework confines acids as evidenced by carbonyl group absorption bands of CH_3COOH (1709 cm^{-1}) and CF_3COOH (1782 cm^{-1}) along with CF_3 stretching vibration bands (1211 and 1170 cm^{-1}).

Anions of these acids are powerful Bronsted bases capable of proton abstracting from the coal framework. Weakly nucleophilic anions (NO_3^- , BF_4^-) are confined in a lattice by ionic bonds, likely, at the cost of formation of stable ion pairs with carbon cations.

Carbonization in an argon atmosphere. Thermal stability of modified coals is significantly reduced. Essentially, all newly formed structural centers undergo disruption at a temperature below 400 °C thus providing the more high yield of volatiles (30 ± 3 % as against 5% for the starting coal). Although the thermolysis behaviour, as illustrated by differential thermogravi-metry (DTG) curves, is specific for each individual reagent, the common trends are revealed reasonably well. Low temperature (below 140 °C) DTG peaks is caused by removal of compounds (acids, water) captured by voids pores in the coal framework. At the temperature interval from 140 to 400 °C a portion of covalent bonds, primarily in nitrogen- and oxygen-containing groups and

aliphatic fragments, is disrupted. Within the same temperature range the destruction of ion pairs occurs, e.g. intra-lattice BF_4^- anions convert completely to BF_3 detectable in gaseous products by IR-spectroscopy.

Carbonization with KOH. Impregnation of modified material with activating agent (KOH) is accompanied by partial breaking of C-O and C-C bonds in framework-forming organic chains and formation of additional reaction centers involving alkali metal cations. As a consequence, a number of new bands detectable only in KOH - impregnated material, arise in IR - spectra. Unlike the starting coal, the thermal destruction of modified material proceeds at higher rates to give volatile products almost in 50% yield. The pattern of thermolysis at a temperature below 500 °C changes essentially as evidenced by appearance of new peaks in the DTG-curves. It is under heating to 500 °C that the "spatial skeleton outline" of incipient carbon lattice is shaped. The number of peaks and their positions on the temperature scale depend on the nature of the reagent used for restructurization of the starting coal. The Table illustrates the effect of the nature of the reagent on specific surface area of carbonized material, all other factors being the same (850 °C, 2 hr, KOH/coal weight ratio 1,5 g/g).

As a conclusion, this work suggests that the change in the mechanism of heat-initiated reactions provides an efficient way for exerting the control over the properties of activated carbons derived from the carbonization of coals.

Table. Surface area development under chemical activation.

Restructurizing agent	Reagent concentration, mol/kg	BET surface area, m ² /g
none		400
$\text{HNO}_3\text{-(CH}_3\text{CO)}_2\text{O}$	20	1500
$\text{HNO}_3\text{-(CH}_3\text{CO)}_2\text{O}$	100	1200
HNO_3	20	1600
$\text{HNO}_3\text{-H}_2\text{SO}_4$	20	1800

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