

NEW FOSSIL PRECURSORS FOR ACTIVE CARBON

N.V. Bodoev, R. Gruber¹, V.A. Kucherenko², J.-M. Guet³, A.P. Kozlov, N. Cohaut³, O. Heintz⁴.

Institute of Carbon Material Chemistry, SB RAS, Kemerovo 650099, Russia

¹*Laboratoire de Thermodynamique et d'Analyse Chimique, Universite de Metz, 57045, France*

²*Institute of Physical Organic and Coal Chemistry, NASU, Donetsk 340114, Ukraine*

³*Centre de Recherche sur la Matière Divisée, rue de Chartres, 45067 Orlean Cedex 2, France*

⁴*I.U.T., Departement Chimie, rue V.Demange, 57400 Saint-Avold, France*

Introduction

The purpose of this study was to estimate the possibility of active carbon preparation from sapropelitic coals. Sapropelites are peculiar raw materials of active carbons because they combine properties of fossil coals and long-chain polymers like polyethylene¹. Sapropelitic coals are very dispersed but represent a great quantity of fossil energy (i.e. stocks in Siberia are about 300 milliards tons)². Thus, these coals are interesting from an economic point of view. In present research sapropelitic coals were used as the precursor for the adsorbent production by traditional and untraditional methods.

Experimental

Semicoking and semicoke activation procedures.

Coal sample (50 g) was placed in quartz vessel which was then heated at rate 2.5 °C/min to temperature of 520 °C. This temperature was maintained for one hour. Liquid product obtained from coal was collected in the cooled retort. The remaining semicoke was cooled. Semicoke sample (5 g) was placed in quartz test-tube (i.d. 21 mm) supplying with two tubes (i.d. 5 mm). One tube served as outlet of off-gas and other one provides the steam inlet to the bottom. Having placed into a muffle at 450 °C test-tube was heated to 820 ± 10 °C within 20 min and maintained for one hour with constant steaming.

Modification procedures.

A sapropelite sample (~1 g) was dried (2 hr, 105 ± 5 °C) and cooled, then mixed with the definite quantity of reactant, and kept during required period of interaction. After that, a modified sapropelite was isolated by either water hydrolysis, three - fold decanting with large excess of water (250 cm³/g), or washing with benzene (10 cm³) and twice by ether (15 cm³). The final sapropelite solid was dried at room temperature till no change in weight is observed. The weight uptake, $\Delta m(\%) = 100(m - m_0)/m_0$, and the volume increase as $\Delta V(\%) = 100(v - v_0)/v_0$ were measured.

Results and Discussion

It was carried out semicoking of six sapropelitic coal samples of various coalification ranks from Peat up to Bituminous. The contents of a hydrogen changed from 10.7 % to 4.7 % (daf).

Gaseous and liquid semicoking products were investigated. The main products of semicoking gas were carbon oxide and dioxide, hydrogen sulfide, light alkanes and olefines. Semicoking tar was separated by column chromatography and distillation. Aliphatic compounds were the main part of tar. Alkylaromatic compounds and normal aliphatic ketones were secondary parts of tar. It was found that the aromatic compound content of sapropelite tar increases with growth of coalification rank of sample.

Activation of sapropelite semicokes was carried out (water steam, 820 degrees Celsius). Samples of active coals were analyzed by thermogravimetry, FTIR, SAXS and BET surface area determination. The BET area of active sapropelite semicokes varied from a few square meters to 455 square meters per gram.

Chemical modification

Other way of preparation of active carbon from sapropelite was a combination of low temperature modification and chemical activation. Detail investigating the influence of chemical modification upon structural alteration of sapropelite was made with the Taimylyr sapropelite.

The concentrated sulfuric acid, and fume HNO₃ (≥ 98 %), H₂SO₄ - SO₃ mixture or acetic anhydride (Ac₂O - HNO₃) mixture at room temperatures were used as modifying reagents. The special attention was given to the (Ac₂O - HNO₃) mixture as a new reagent of modification. This mixture forms acetylnitrate:
 $\text{HNO}_3 + \text{Ac}_2\text{O} = \text{NO}_2\text{AcO} + \text{AcOH}$ with equilibrium shifted to the right at room temperatures.

When varying the reactant/coal ratio, the weight uptake as well as volume of modified sapropelite have increased as shown of Table 1.

Table 1. Weight and volume changes of sapropelite after modification

	Method of isolation	NO ₂ AcO /coal ratio, mol/kg			
		10	15	20	50
Δm, %	aprotic solvents	20	21	22	21
	hydrolysis	2	2	4	4
ΔV, %	aprotic solvents	46	51	62	32
	hydrolysis	19	19	19	14

By this data, it is shown that:

- reactive particles penetrate into the sapropelite framework and lead to swelling and weight uptake;
- a some portion of inserted particles is weakly fixed within framework and may be removed by water hydrolysis; the treatment of aprotic solvents (benzene + ether) does not affect these particles.

In order to inform the modification conditions, the 20 h period and the 20 mol/kg ratio were selected for all modifying reagents.

Structural alteration

Comparing DRIFT spectra and deconvolution spectra of different spectral regions, the essential structural changes have been observed.

- An aliphatic nitro compounds appears within the sapropelite macrostructure. The stretching vibrations of NO₂ - groups bonded with alkane chains are observed at 1555 cm⁻¹ (asymmetric) and 1375 (symmetric) cm⁻¹. Besides, the deformation vibrations of C_{alk} - N bonds (849 cm⁻¹) is registered.
- The ester and/or ether groups are formed, and the C - O band at 1277 cm⁻¹ appears. That may be because of either acetoxylation with forming - C - O - C(O) - CH₃ groups or inserting O - atoms into aliphatic networks of sapropelite. The free molecules of NO₂AcO within framework are absent; the band at 1798 cm⁻¹ corresponding to C = O vibrations of acetylnitrate is not observed.
- It is also probable to appear structural fragments with C = N bonds (1589 cm⁻¹) or nitrozo-compounds. As a consequence, the 1600-1500 cm⁻¹ region is transformed. Evidently, the nitration occurs in the first place and transforms the alkane framework of sapropelite into other, predominantly nitro-alkane, spatial framework. Element analysis (% daf) of modified Taimylyr sapropelite (C - 64.4 ; H - 8.2; N - 4.5 and O - 21.9) are support this conclusion.

Thermolysis of modified sapropelite.

The behavior of sapropelite after modification is changed. The peak of maximum weight loss at 200 °C is increased with growing the NO₂AcO/coal ratio and is shifted towards lower temperatures, namely from 200 °C to 150 °C. The main peak of decomposition of the parent sapropelite (about 420 °C) is not changed in place,

but the rate of weight loss is decreased when increasing a degree of modification. The summary weight loss of modified sapropelite is lower than that of the parent sample, i.e. about 70 % vs 90 %. Probably, the thermoinitiated reactions within 100 - 250 °C region promote polycondensation and/or polymerization processes of forming the secondary organic framework and, by the reason, decrease the summary yield of gaseous and volatile substances.

An additional information concerning the low temperature region (up to 300 °C) was obtained by Bio - Rad Win - IR method. TG and DTG thermograms were obtained by even heating of sample up to 250 °C and subsequent holding at 250 °C. IR spectra of volatile products in process intensive decomposition of modified coal were recorded. The main volatile products were CO₂ (peaks at 2358 and 2309 cm⁻¹), NO₂ (peaks at 2973, 2940 cm⁻¹ and 2238, 2199 cm⁻¹), water (area 4000 - 3400 cm⁻¹) and the low molecular nitroproducts containing C = O groups (1777 and 1796 cm⁻¹).

Chemical activation

The combination of modification with subsequent chemical activation allows to obtain carbon materials with high surface areas. When using the KOH/sample ratio equal 1 g/g, specific surfaces more than 1000 m²/g may be obtained. If increasing the KOH/sample ratio up to 1.5 g/g, the final surface area of sample obtained by NO₂AcO pretreatment grows until 1130 m²/g. Two independent methods, SAXS and BET determination, show very close data (Table 2).

Table 2. Surface area (m²/g) of active carbon.

Modification reagent	Specific surface by	
	BET	SAXS
NO ₂ AcO	1130	1200
H ₂ SO ₄	1460	1600

Conclusions

- Water steam activation of sapropelite semicokes leads to carbon materials with S < 500 m²/g.
- Low temperature modification strongly affects the surface area development under chemical activation with KOH.
- Chemical activation of modified sapropelites results in active carbons with high surface area ranged between 1000 - 1600 m²/g. These results obtained with BET area determination are confirmed by SAXS analysis.

References

- Bodoev, N.V., Guet, J.-M., Gruber, R., Dolgoplov, N.I., Wilgelm, J.-C. and Bazarova, O. Fuel 1996, 75, 839.