Modification of the surface layer of carbon nanomaterials using the Diels–Alder reaction

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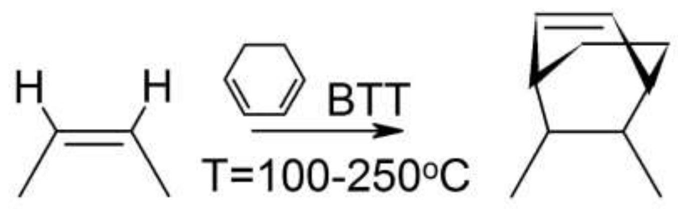
Carbon nanomaterials (CNM) have high specific surface area and electrical conductivity. These CNM include nanoporous carbon sorbents those have unique mechanical properties and are non-toxic. So, one can use the CNM to solve the problems in chemical technology, ecology, and medicine. The chemical properties of CNM allow modifying the surface layer to improve material characteristics and obtain a variety of functional materials. The Diels-Alder (DA) reaction is very selective and runs between a diene and an unsaturated compound, which is a dienophile. The CNMs can contain both isolated carbon-carbon double bonds and conjugated carbon–carbon bonds, i.e., they can react with DA as both diene and dienophile. This work aims to study the ways of hydrophobization of the surface of various carbon nanomaterials: multi-walled carbon nanotubes (MWCNTs), activated carbon (AC), and carbon fibers (CF). The reactivity of active CNM centers in the reaction with 1,3-Cyclohexadiene (CHD) was investigated to address this issue. Barothermal treatment (BBT) was used for effective modification, and the sample of CNM was autoclaved with CHD at 90, 150, 175, 200, 225 and 250 °C. Samples were investigated by miscellaneous methods, including SEM, adsorption of N_2, TG/DTG and TPD MS.

Hydrophobization of the surface of carbon nanomaterials using 1,3-cyclohexadiene



Characterization of modificated carbon nanomaterials

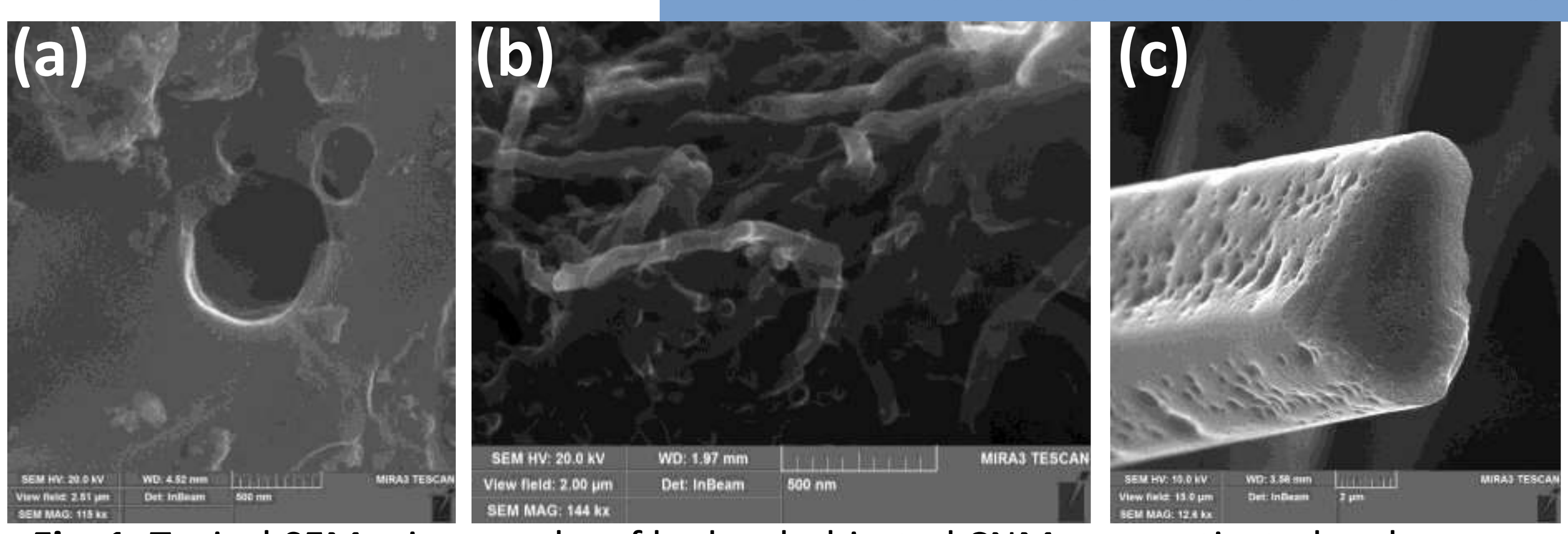


Fig. 1. Typical SEM micrographs of hydrophobized CNMs: **a** – activated carbon, **b** – multi-walled carbon nanotubes, **c** – carbon fibers (BTT with 1,3-cyclohexadiene at 200°C).

Table 1. Texture parameters of initial and hydrophobizated activated carbons

Sample	S_{BET}, m²/g	S_{micro}, m²/g	S_{meso}, m²/g	V_{tot}, cm³/g	V_{micro}, cm³/g	V_{DR}, cm³/g
AC	841	750	91	0.444	0.305	0.326
AC-CHD90	712	616	95	0.473	0.259	0.303
AC-CHD150	532	446	86	0.368	0.227	0.268
AC-CHD200	245	190	54	0.199	0.081	0.106
AC-CHD250	284	192	92	0.220	0.082	0.110

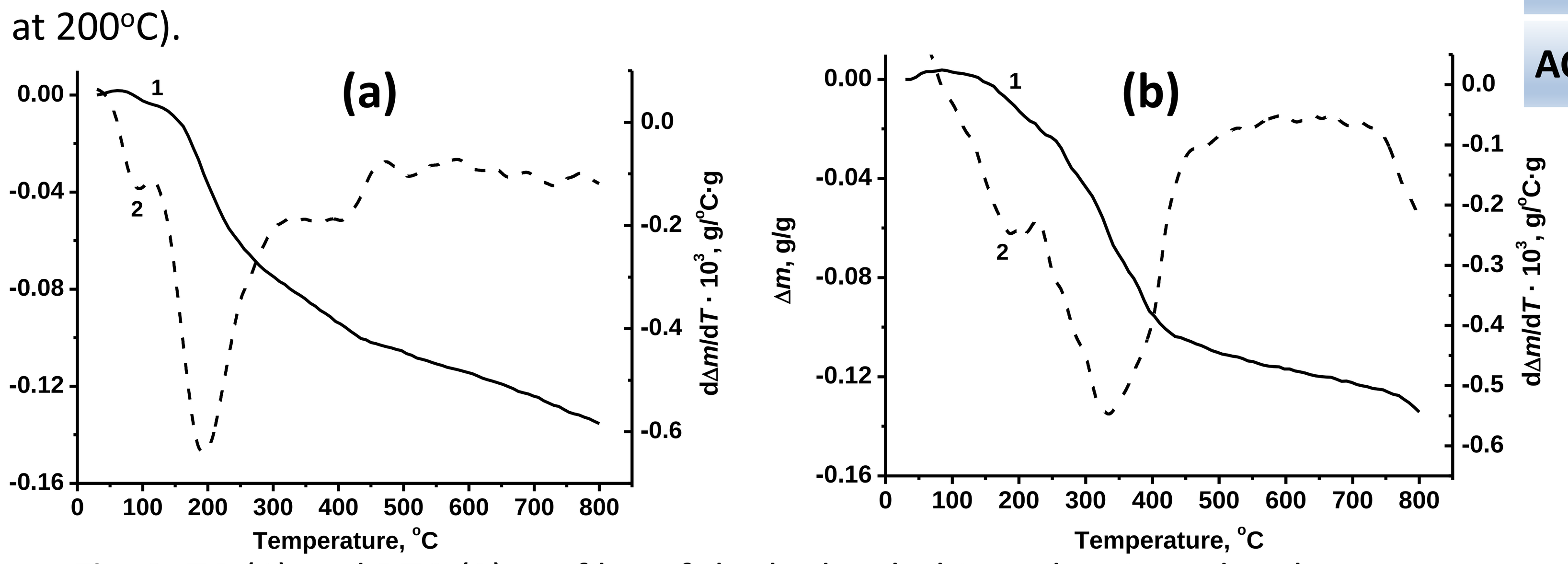


Fig. 2. TG (1) and DTG (2) profiles of the hydrophobizated activated carbons : **a** – AC-CHD150, **b** – AC-CHD225.

Table 2. TG/DTG parameters of hydrophobizated activated carbons

Sample	Δm, %	T_{m1}, °C	$Δm_1$, %	T_{m2}, °C	$Δm_2$, %
AC-CHD90	7.68	209	1.47	256	6.21
AC-CHD150	7.38	201	4.99	357	2.39
AC-CHD175	7.63	205	3.47	399	4.16
AC-CHD200	9.43	209	2.76	380	6.67
AC-CHD225	10.36	209	3.56	372	6.80
AC-CHD250	10.22	185	3.04	341	7.18

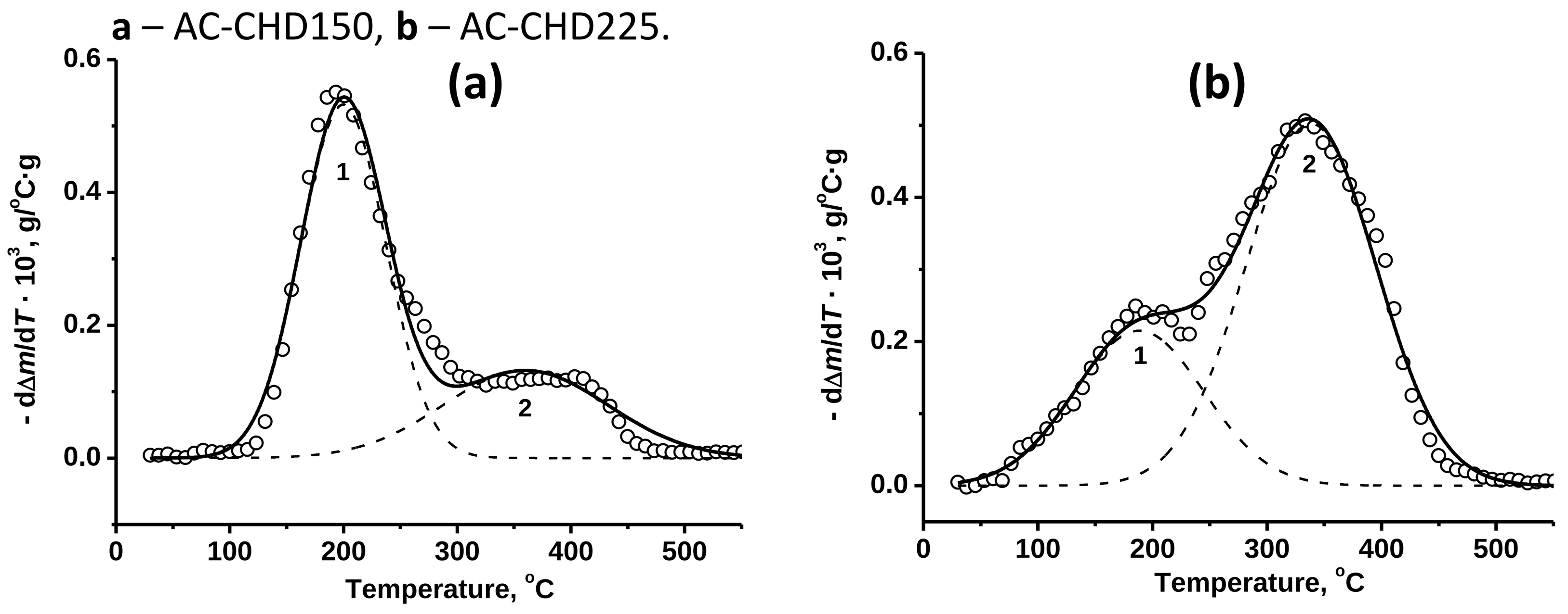


Fig. 3. Deconvolution of DTG effect for the hydrophobizated activated carbons : **a** – AC-CHD150, **b** – AC-CHD225.

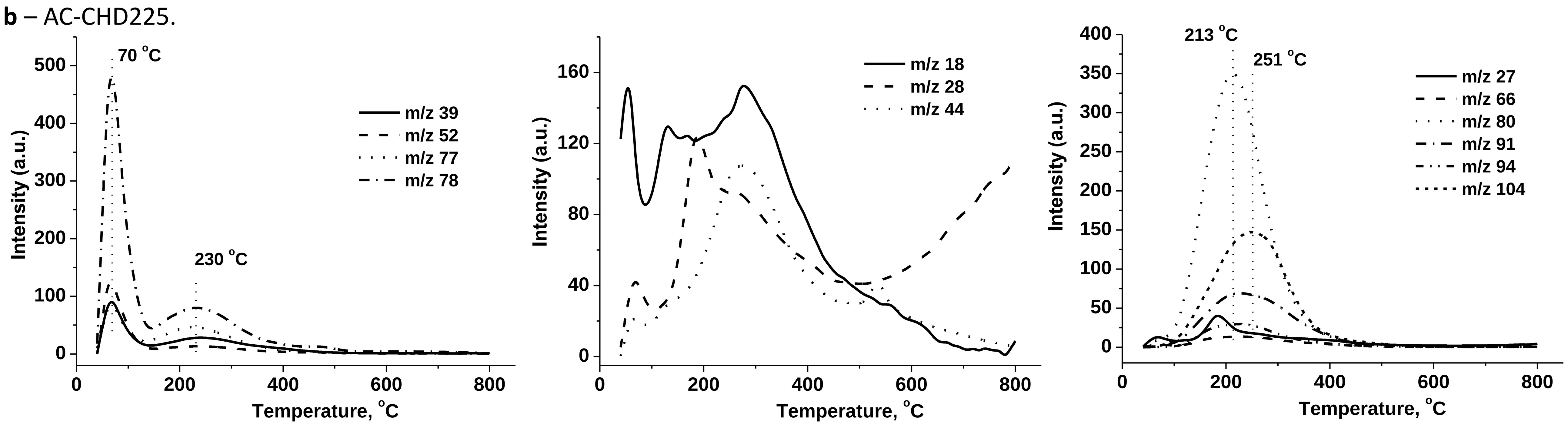


Fig. 4. Typical TPD MS profiles of the hydrophobizated activated carbons (sample AC-CHD225).

Conclusions. TGA proved two temperature forms of chemosorbed 1,3-cyclohexadiene that are formed after the modifying. The first form is sourced form Diels-Alder grafted residues and decomposed between 100 and 300 °C. Its highest concentration, up to 0.63 mmol/g, was reached for BTT with 1,3-cyclohexadiene at 150 °C. Thermal decomposition of the second form occurs above 350–400 °C. Its highest concentration, up to 0.9 mmol/g, was reached for BTT with CHD at 250 °C. This form is the product of thermal destruction of chemosorbed spices and the partial pyrolysis of 1,3-cyclohexadiene. Under TPDMS control, the pyrolysis of the modified ACs, MWCNTs and CFs proved the formation of chemisorbed CHD. The products of their partial degradation and dimerization are also found. The Diels-Alder process was accompanied by tandem red-ox reactions caused the strong reducing properties of the CNMs surface. In sum, the Diels-Alder reaction is an effective method for the functionalization of the surface of carbon nanomaterials.