Effective alcohol dehydration using solid acid catalysts prepared from nanoporous activated carbon fibers

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Nanosized carbon materials are widely used in adsorption [1,2], catalysis [3] and in energy conservation systems [4]. In recent years, the chemistry of nanoporous carbon materials (NCMs) is evolving at an accelerated pace, in particular due to the unique properties of the carbon matrix. NCMs are widely used in catalysis because they are easy to separate from the reaction mixture and regenerate. In addition, they can be obtained from renewable natural raw materials. Therefore, the search for new effective methods for introducing acid groups into the surface layer of the NCMs is an urgent problem. This work is devoted to the functionalization of nanoporous carbon fiber (NCF) by sulfur-containing groups and the study of thermodesorption and catalytic properties of the obtained materials.

The starting NCMs were taken from carbon cloth of commercial trademark Busofit RT 055 (Sokhim Resources Co., Svetlogorsk, Belorussia). The surface of carbon fiber made of viscose was modified with sulfur vapor in the temperature range of 400-800° C, followed by oxidation of the obtained materials with hydrogen peroxide, resulting in samples of carbon fiber containing sulfur-containing acid groups on the surface.These synthesis temperatures are used to denote the synthesized materials. The synthesized samples were studied in a model reaction - gas-phase dehydration of isopropanol with the formation of propylene.

Methods:

- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- Chemical Analysis (C.A.)
- Thermogravimetric analysis (TGA)
- Thermoprogrammed desorption with IR registration of products (TPD IR)
- Thermoprogrammed desorption mass-spectrometry (TPD MS)

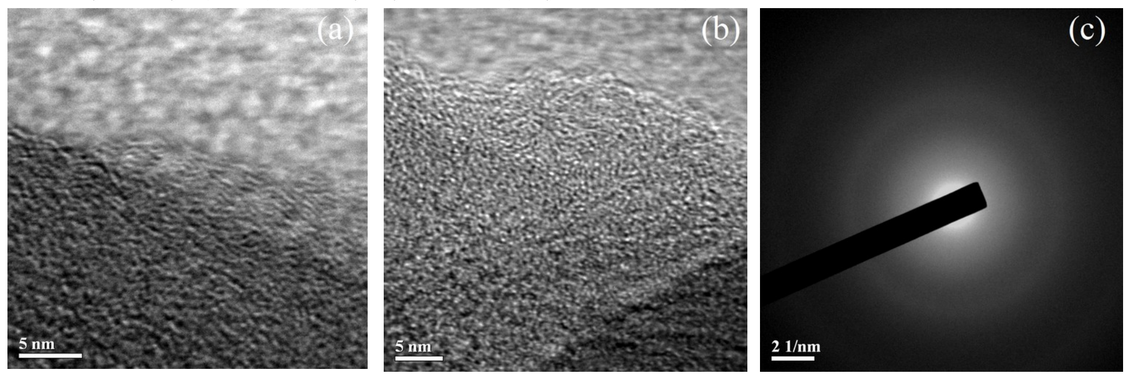

FIGURE 1. TEM micrographs (a, b) and SAED pattern of the Busofit sample (c).

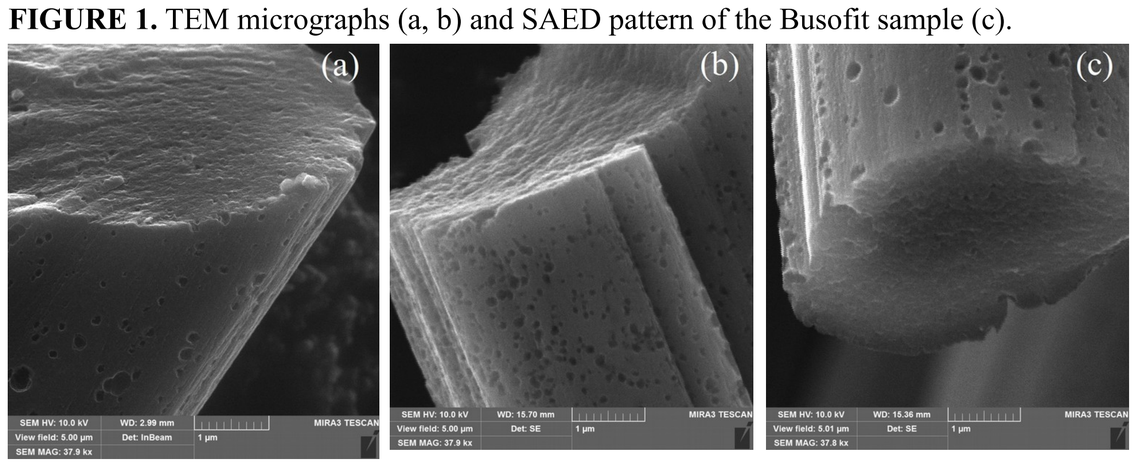

FIGURE 2. SEM micrographs: (a) Busofit, (b) Bus/S1/500, (c) Bus/S1/800.

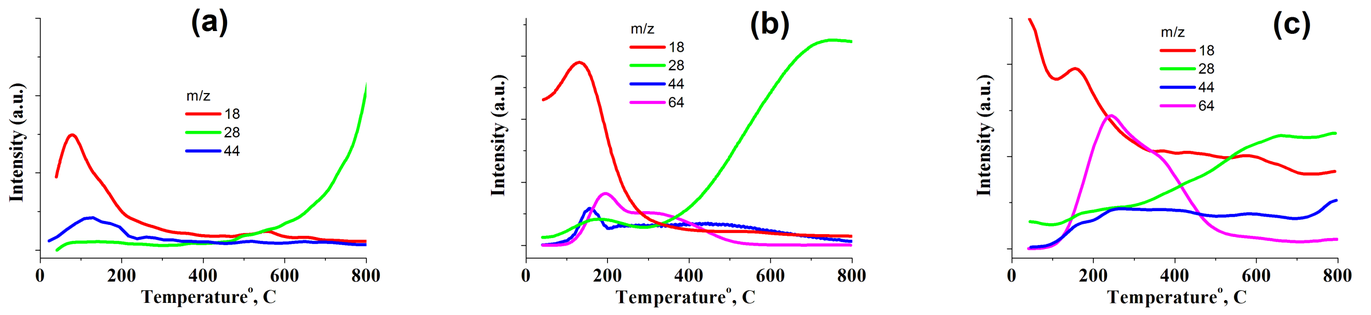

FIGURE 1. TPD MS profiles for Busofit (a) and Bus/S1/500 (b) and Bus/S2/500 (c).

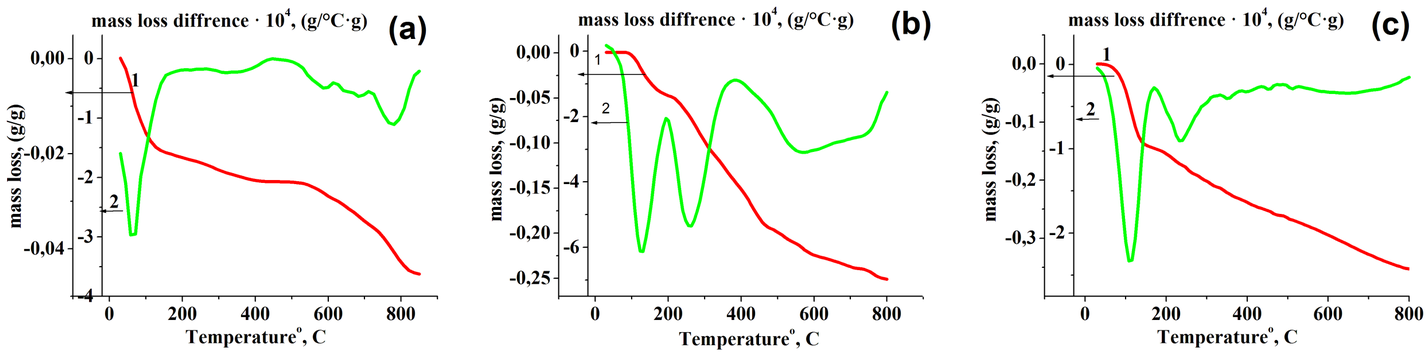

FIGURE 2. TGA: (1) TG and (2) DTG for Busofit (a) and Bus/S1/500 (b) and Bus/S2/500 (c).

Table1. The temperature intervals of sulfogroups desorption from the surface of the NCF Busofit samples obtained by S1 method (ΔT), the temperature of the maxima of the low- and high-temperature desorption region (T_{max1} and T_{max2}), respectively, determined by the TPD MS method

Sample	ΔT, °C	T_{max1}, °C	T_{max2}, °C	C, mmol/g
Bus/S1/400	110-550	245	400	4,05
Bus/S1/500	100-550	190	330	3,82
Bus/S1/600	100-550	195	310	2,97
Bus/S1/700	100-550	211	330	1,15
Bus/S1/800	120-500	211	290	0,53

Table 2. The temperature intervals of sulfogroups desorption from the surface of the NCF Busofit samples obtained by S2 method (ΔT), the temperature of the maxima of the low- and high-temperature desorption region (T_{max1} and T_{max2}), respectively, determined by the TPD MS method

Sample	ΔT, °C	T_{max1}, °C	T_{max2}, °C	c, mmol/g
Bus/S2/400	90-550	195	325	5,66
Bus/S2/500	100-550	225	335	4,73
Bus/S2/600	90-550	185	310	3,57
Bus/S2/700	100-550	230	335	1,64
Bus/S2/800	100-550	216	320	1,51

Table 3. Temperatures of complete conversion ($T_{100\%}$) of isopropyl alcohol into propylene for three heating-cooling cycles

Sample	$T_{100\%}$, °C					
	Method S1			Method S2		
	I cycle	II cycle	III cycle	I cycle	II cycle	III cycle
Bus/400	150	150	150	175	180	190
Bus/500	170	170	170	145	145	145
Bus/600	160	160	160	140	140	140
Bus/700	190	190	190	150	155	155
Bus/800	220	225	235	180	180	180

Conclusions

1.The surface of carbon fiber made of viscose was modified with sulfur vapors in the temperature range of 400-800° C, followed by oxidation of the obtained materials with hydrogen peroxide, resulting in samples of carbon fiber containing sulfur-containing acid groups on the surface.

2. Chemical analysis showed that the concentration of sulfur in the synthesized samples is in the range of 0,5-5,6 mmol/g.

3. It is shown that the obtained materials are characterized by significant thermal stability and have high catalytic activity - complete conversion of isopropanol into propylene is observed at a temperature of 140-180° C.

4. It was found that the modification of carbon fiber by the method of S2 leads to obtaining more active catalysts, using which the temperatures of the dehydration reaction of isopropyl alcohol are reduced by 20-55ºC compared with the method of S1.

Acknowledgments

This work is supported by the Ministry of Education and Science of Ukraine, Grant Nos. [0111U006260], [0114U003554], [0116U002558], and [0119U100167].

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