Catalysts of dehydration of isopropyl alcohol based on chlorinated carbon fiber

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Carbon nanomaterials have unique properties, which are determined by their surface chemistry and developed porous structure [1]. It is important to develop methods for purposeful surface modification of carbon materials, which opens the way for the creation of adsorbents with high selectivity, specific carriers of catalysts and catalysts with a developed surface [2].

This work is devoted to the study of chlorination of carbon fiber based on polyacrylonitrile (PAN) with carbon tetrachloride and the possibility of using chlorine-containing precursors to obtain sulfur-containing fiber and to study the catalytic properties of the obtained samples.

As a starting material was used industrial nanoporous carbon fiber, made by carbonization of polyacrylonitrile (NCFPAN) with subsequent activation by water vapor. The surface of carbon fiber was modified with carbon tetrachloride followed by substitution of chlorine-containing groups with sulfur-containing groups. Chlorination was performed at temperatures of 300, 450 and 600°C. These temperatures are indicated in the names of the samples. Substitution of chlorine-containing groups was conducted by treating the samples with sodium sulfide (Na_2S) and sodium mercaptoacetate (MA). The synthesized samples were studied in a model reaction - gas-phase dehydration of isopropanol with the formation of propylene. The degree of catalytic activity was the temperature of 50% conversion of isopropanol to propylene ($t_{50\%}$).

METHODS:

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

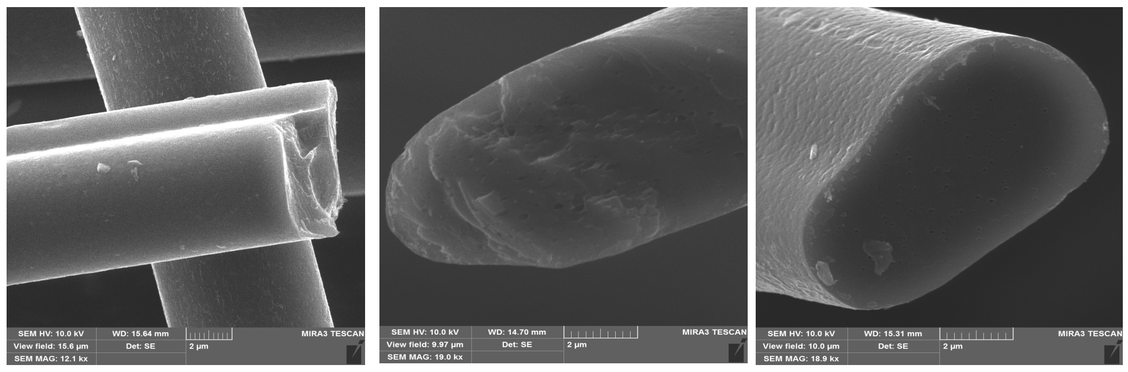

FIGURE 1. CEM microphotographs of the initial carbon fiber.

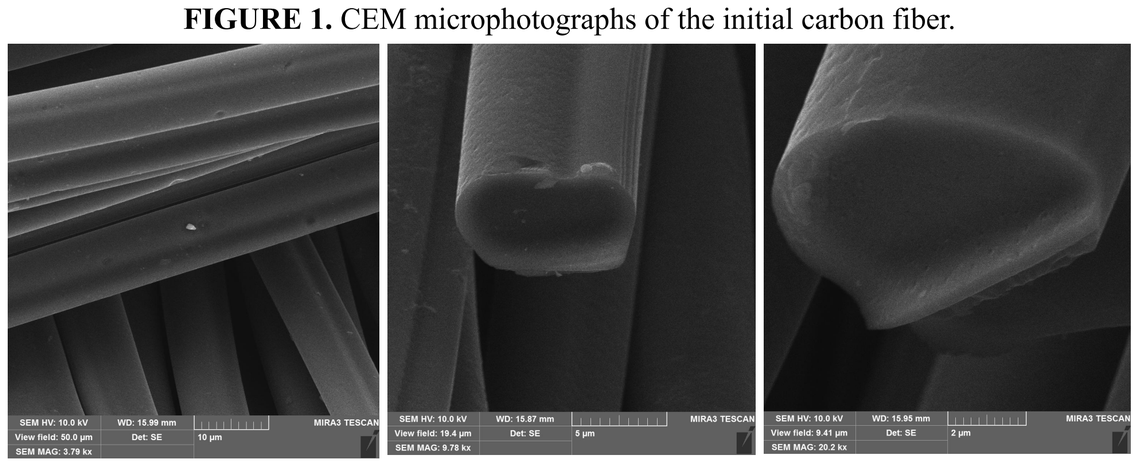

FIGURE 2. SEM microphotographs of chlorinated carbon fiber.

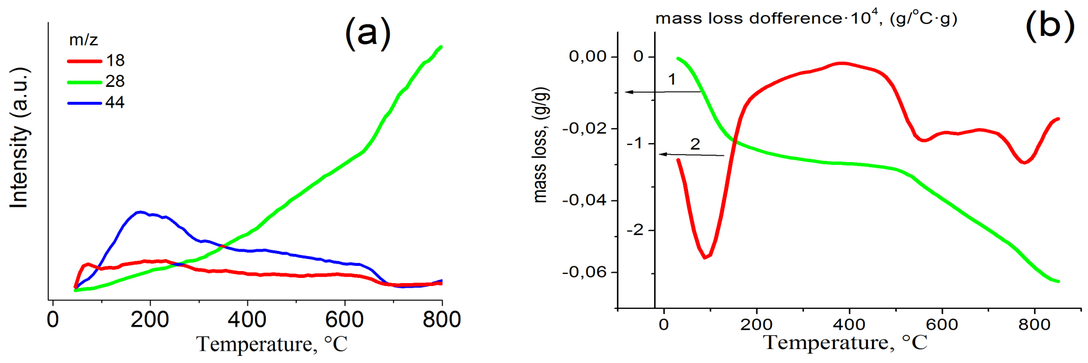

FIGURE 3. TPD MS (a) and TGA (b) profiles of initial carbon fiber.

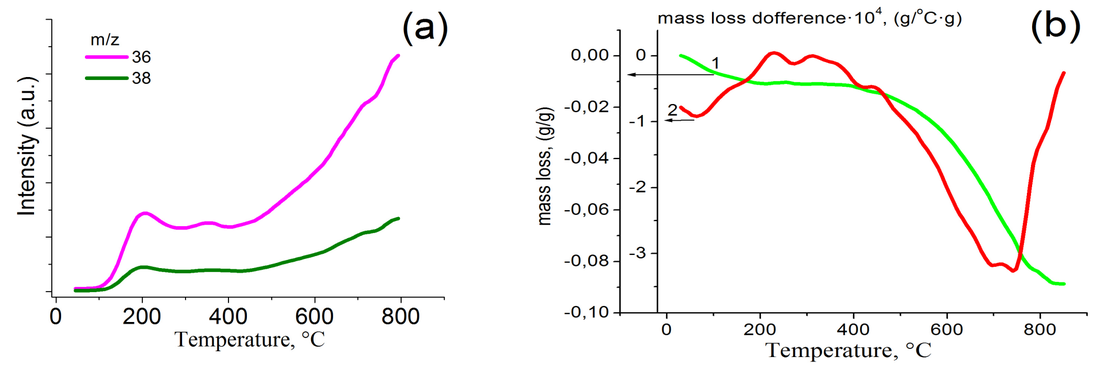

FIGURE 4. TPD MS (a) and TGA (b) profiles of chlorinated carbon fiber.

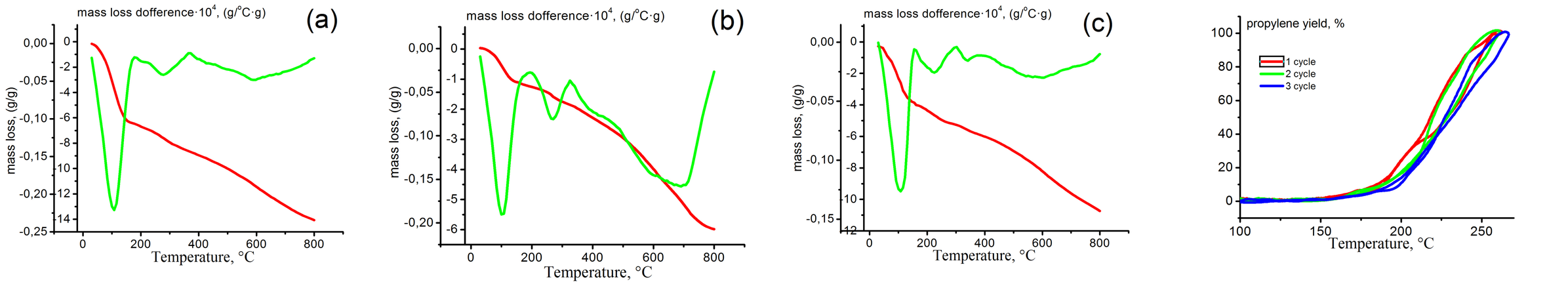

FIGURE 5. TGA: (1) TG and (2) DTG profiles of sulfonated carbon fiber (on the example of samples treated with sodium sulfide): NCFPAN/$CCl_4$300/Na_2S (a), NCFPAN/$CCl_4$450/Na_2S (b), NCFPAN/$CCl_4$600/Na_2S (c).

FIGURE 5. Catalytic activity of modified carbon fiber samples for three heating-cooling cycles (sample NCFPAN/$CCl_4$300/Na_2S).

Conclusions

1. Chlorination of carbon fiber at different temperatures was performed and active chlorine-containing precursors were obtained, in which chlorine is able to be replaced by sulfur-containing groups.

2. The thermal stability of modified samples was investigated.

3. The catalytic activity of the modified fiber was studied. It was found that the catalytic activity of the modified fiber depends mainly on the chlorination temperature and for the most active samples $t_{50\%}$ is 250°C.

Acknowledgments

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References

1. Park S.-J. *Carbon Fibers*. Dordrecht. Springer. 2015.

2. Li D., Ma X.. *Cellulos.* 2013. **20** (4). 1649-1656

Table1. Total weight loss (Δm_{tot}), the temperature intervals (ΔT) of sulfogroups desorption and temperatures of their maximum (T_{max}), sulfur concentration (c(S)) and catalytic activity ($t_{50\%}$) of modified carbon fiber samples, determined by the C.A. and TGA methods

Sample	$\Delta m_{tot,}$ g	ΔT, ° C	T_{max},° C	c(S), mmol/g	$t_{50\%}$, °C
NCFPAN/$CCl_4$300/Na_2S	0,23	175-370	275	0,32	215
NCFPAN/$CCl_4$450/Na_2S	0,21	190-330	270	0,24	275
NCFPAN/$CCl_4$600/Na_2S	0,14	160-300	225	0,20	290
NCFPAN/$CCl_4$300/MA	0,12	180-370	250	0,31	220
NCFPAN/$CCl_4$450MA	0,21	160-295	210	0,28	250
NCFPAN/$CCl_4$600/MA	0,20	165-320	235	0,22	285