

Investigation of Oxidation and Modification of the Carbon Composite Material by Hydrolyzed Compounds of Antimony (V)

I. V. SHEMYAKINA¹, L. M. LEVCHENKO², V. V. MUKHIN¹ and E. E. YURLOVA¹

¹JSC “Novosibirsk Chemical Concentrates Plant”,
Ul. B. Khmel'nitskogo 94, Novosibirsk 630110 (Russia)

E-mail: or@nccp.ru

²Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)

E-mail: luda@che.nsk.su

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Abstract

Oxidation and modification processes in the carbon composite material of “Tekhnosorb” grade are investigated. Carbon materials, oxidized and modified with the compounds of antimony (V) (NUMS-O, NUMS-Sb), are examined by means of thermal analysis, X-ray diffraction. It is established that antimonic acid can be synthesized on the surface of HUMS-O either in the crystal form and in the amorphous one, depending on the temperature of oxidation of the carbon surface.

INTRODUCTION

In order to solve one of the most important problems of chemical industry, *i.e.*, to obtain lithium salts of special purity, it is necessary to extract admixtures to a level of $(10-0.05) 10^{-6} \%$.

Selective extraction of metal (sodium, calcium) admixtures from concentrated solutions of lithium chloride is possible only with the adsorption method in which the decisive factor is the application of a definite sorbent. Because of this, development of new sorbents which are selective to alkaline metals and alkaline earths, especially to sodium and potassium, becomes urgent. Development of a sorbent implies both the choice of its basis and subsequent processes to modify the basis.

In order to develop technological methods of obtaining the sorbent selective to alkaline metals and alkaline earths, we chose a carbon material manufactured by the Omsk Technological Design Institute of Industrial Carbon, SB RAS (TDIIC) as the basis for the sorbent. Unlike the known activated carbon

materials, the synthetic carbon composite material (CCM) of Tekhnosorb grade has several advantages, namely, large specific surface, high mechanical strength, purity (low microimpurity content), meso-porous structure.

Oxidized coal is known to behave like a special cationite in the H form. The formation of cation exchange modification of active coal during oxidation with air was discovered for the first time in 1929 by the authors of [1, 2]. It was shown that carbon sorbents with cation exchange properties can be obtained by treating active coal with oxidizing agents in the gas and liquid phases [3, 4]. Because of this, choice of modes and procedures of carbon surface oxidation was the first step of investigation of CCM.

Since the oxidized carbon basis itself is not a selective sorbent, it was necessary to investigate the processes of modification of NUMS-O by hydrolyzed compounds of antimony (V) for the purpose of obtaining sorbents possessing high adsorption capacity towards sodium and calcium.

The choice of antimony (V) as a modifying agent for hydrolyzed compounds is explained by the formation of difficultly soluble compounds of alkaline metals. The strength of the surface complexes is such that some oxidized coal samples modified with Sb(V) can be used to purify concentrated LiOH and LiCl solutions from metal admixtures [5–9].

Methods of obtaining selective sorbents with the use of hydrolyzed compounds of antimony as a modifier deposited on a support (zeolite, silica gel, aluminium oxide, ion exchange resins) were described, as well as subsequent use of the sorbents to purify lithium chloride solutions from sodium admixture [10, 11]. The adsorption capacity of sorbents with respect to sodium depends on the structure of hexahydroxo-antimonic acid.

At present, amorphous and crystalline hydrated oxides of pentavalent antimony, or the so-called hydrolyzed antimony compounds, are rather well investigated [12–21]. It is known that hexahydroxoantimonic acid exists in the form of $n\text{H}[\text{Sb}(\text{OH})_6]$ [14, 19, 21]. In addition, one distinguishes amorphous polyantimonic acid of the composition $\{\text{H}[\text{SbO}_{x/2}(\text{OH})_{x-6}]\}_n$ and crystal polyantimonic acid (ACA) – $\{\text{H}[\text{SbO}_{6/2}]\}_n$. However, it is still unknown in what form antimonic acid exists on a carbon material, though the sorption capacity with respect to sodium is substantially dependent on the form of its existence.

The goal of the present investigation is to study the properties of carbon sorbents (NUMS-O and NUMS-Sb) oxidized and modified by hydrolyzed compounds of antimony (V) at different temperatures.

EXPERIMENTAL

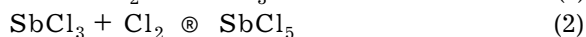
The basis for obtaining sorbents was the carbon-carbon composite material (CM) of Tekhnosorb-1 grade (TU-038-41538-94) manufactured at EDITC; the characteristics of this material are: bulk density, $r = 0.45\text{--}0.68$ g/cm³; total pore volume: $V_{\text{sp}} = 0.71\text{--}1.1$ cm³/g; specific surface $A_{\text{sp}} = 400\text{--}450$ m²/g, particle size 1–1.2 mm.

Weighed portions of the CM were oxidized for 1 h in the air flow of 15–20 l/min in

Nabertherm L9/12/S27 furnace with thermal control. The adjusted temperature range was 200–600 °C with a step of 50 °C. After cooling in the air, samples were weighed to determine the loss. The samples of NUMS-O (oxidized) were obtained at 200, 250, 300, 350, 400, 450, 500, 550, 600 °C.

To study the subsequent modification of different NUMS-O by hydrolyzed compounds of antimony (V), we used antimony (V) pentachloride.

Synthesis of antimony (V) pentachloride was carried out according to [22]. Depending on temperature and chlorine flow rate, a mixture of SbCl_5 and SbCl_3 is formed during chlorination of metal antimony; this mixture can be used as the starting one to obtain antimony (V) chloride:



Small amounts of antimony were chlorinated in a three-throw tube. A weighed portion was placed in the first bend. A mixture of chlorides which was formed under slight heating was carried into the second bend of the tube. After termination of the chlorination process, chlorine was passed through the tube for some more time. The formed antimony (III) chloride was transformed into antimony (V) chloride, which is liquid at room temperature.

Chlorine was obtained by electrolysis of the sodium chloride solution, purified and dried by passing through a hydroseal and concentrated sulphuric acid. Liquid antimony chloride was collected in a special bottle with a sealing plug.

Modification of all the NUMS-O samples was carried out using SbCl_5 under identical conditions. Weighed portions (5.0 g) of the samples were placed in cone flasks 50 ml in volume, then 2.336 g (1 ml) of SbCl_5 was added into each flask. After 20 min, 1 cm³ of distilled water was added into each flask; the flasks were closed with plugs and left for a week. After that, NUMS-Sb samples were dried at a temperature within 80–100 °C for 3–4 weeks. After that, NUMS-Sb was washed several times with the portions of distilled water at the solid to liquid ratio of 1 : 100, dried at a temperature within 100–110 °C for 4–5 h. After cooling, the samples were weighed and stored in polyethylene bottles with screw-tops.

The obtained sorbents of the NUMS-O and NUMS-Sb rows were examined using thermal and X-ray phase analysis.

Thermal analysis was carried out with the TA-4000 thermal analyzer of Mettler company (Germany) recording mass loss curves (TG), the first derivatives of mass loss curves (DTG), enthalpy change curves DSC (differential scanning calorimetry) and the rate of enthalpy change (the first time derivative of DSC). Sample heating rate was 10.0 °C/min; temperature was varied up to (600 ± 0.2) °C. Weighing range was 0–150 mg with the accuracy of 0.01 mg. To record TG curves, we used a crucible made of aluminium oxide, 40 ml in volume. To measure the heat effect of DSC, aluminium crucible was used; the reference was an empty aluminium crucible. The TG and DTG measurements were carried out in the air, DSC in a tightly closed crucible without any access for air (tightness was achieved by curling the crucible cap).

X-ray phase analysis of NUMS-O and modified NUMS-Sb was carried out with DRON-3 X-ray instrument; recording rate: 2 °/min; CuK_α

TABLE 1

Content of hydrolyzed antimony compounds (Sb_{aq}) in NUMS-Sb at different temperature of oxidation of NUMS-O, $m_{\text{NUMS-O}} = 5.00$ g

$T_{\text{ox}}, ^\circ\text{C}$	Mass, g		Sb _{aq} content, %
	NUMS-Sb	Sb _{aq}	
Initial	6.90	1.90	38.0
200	6.70	1.70	34.0
250	6.86	1.86	37.2
300	6.77	1.78	35.6
350	6.86	1.86	37.3
400	6.21	1.21	24.3
450	6.52	1.52	30.3
500	6.61	1.61	32.2
550	6.85	1.85	37.0

radiation. The samples were ground in an agate mortar and mixed with a binding component (medical Vaseline was used).

RESULTS AND DISCUSSION

The results of analysis, thermal and X-ray structural investigations of NUMS-O and NUMS-Sb at different temperature are shown in Tables 1–3 and Figs. 1–6.

Analysis of the data listed in Table 1 indicates that the content of hydrolyzed antimony (V) compounds on the sorbent varied from 38 to 24 %. The smallest amount of hydrolyzed antimony (V) compounds was observed on the sorbent oxidized at 400 °C.

Temperature maxima of exothermal effects of NUMS-O, NUMS-Sb and mass losses accompanying these effects are shown in Table 2.

Analysis of the mass loss curves for NUMS-O and NUMS-Sb (see Figs. 1–3, a) shows that exoeffects of NUMS-O occur at the maxima of temperature from 70 to 76 °C, and mass loss is 0.25 to 0.91 % of the initial mass of the weighed portion. The second exoeffect is observed at the maxima of temperature within 605 to 664 °C; mass loss is 1.6 to 3.0 %.

Quite a different situation is observed in thermograms of modified NUMS-Sb samples (see Figs. 1–3, b). The maxima of temperature

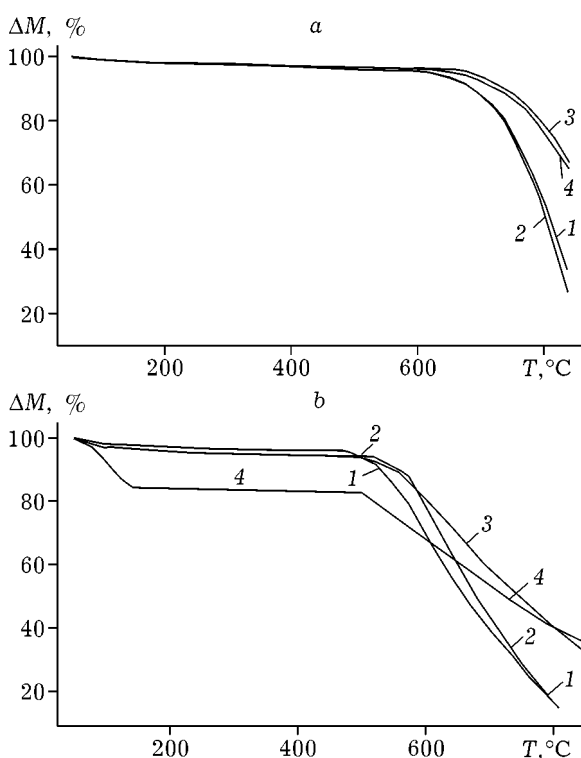


Fig. 1. The curves of mass loss for NUMS-O (a) and NUMS-Sb (b) at different temperatures: 1 - initial, 2 - $T = 200$ °C, 3 - $T = 350$ °C, 4 - $T = 400$ °C.

TABLE 2

Mass loss at the maxima of exoeffects (T_1 , T_2) for NUMS-O and NUMS-Sb

T_{ox} , °C	NUMS-O				NUMS-Sb			
	T_1 , °C	Dm_1 , %	T_2 , °C	Dm_2 , %	T_1 , °C	Dm_1 , %	T_2 , °C	Dm_2 , %
Initial	74.5	0.91	664.0	3.0	100.0	3.84	420.0	6.0
200	75.6	0.91	664.0	3.0	102.6	3.83	438.0	6.0
250	No clear peak		649.0	3.54	78.8	2.92	507.5	7.54
300	No clear peak		641.7	2.9	78.8	2.26	526.0	8.93
350	70.0	0.25	605.0	1.6	90.0	2.95	475.0	7.83
400	70.0	0.29	610.0	2.0	113.3	8.3	495.0	17.5
450	No clear peak		614.0	3.65	71.5	3.04	439.0	9.96
500	No clear peak		593.6	4.73	74.4	2.63	415.6	8.65

of the first exo-effects are observed within the range of 71.5–113.3 °C, that is, at a higher temperature, and mass loss is 2.5 to 8.2 %, which is likely to be connected with the loss of water from hydrolyzed antimony compounds. The maxima of the second exoeffects are observed within the range 415.6 to 526 °C, which is lower than the values for non-modified samples; mass loss is 6.0 to 17.5 %. Elevation of the temperature maximum of the first exoeffect and a decrease in the temperature maximum of the second

exoeffect in the modified samples is connected with the presence of modified antimony compounds on the carbon surface. At first, they coat the surface and prevent destructive oxidation on the carbon surface, then they accelerate these processes getting detached from the surface and capturing the surface oxygen.

The NUMS-Sb sample oxidized at $T = 400$ °C (see Fig. 3, b) exhibits a larger mass loss at the temperature of exoeffect (113.3 °C) than other samples do. After the second exothermal

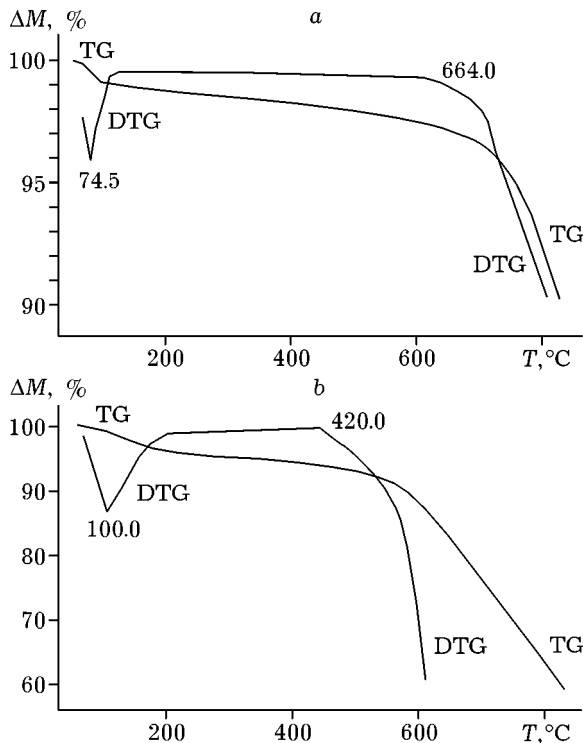
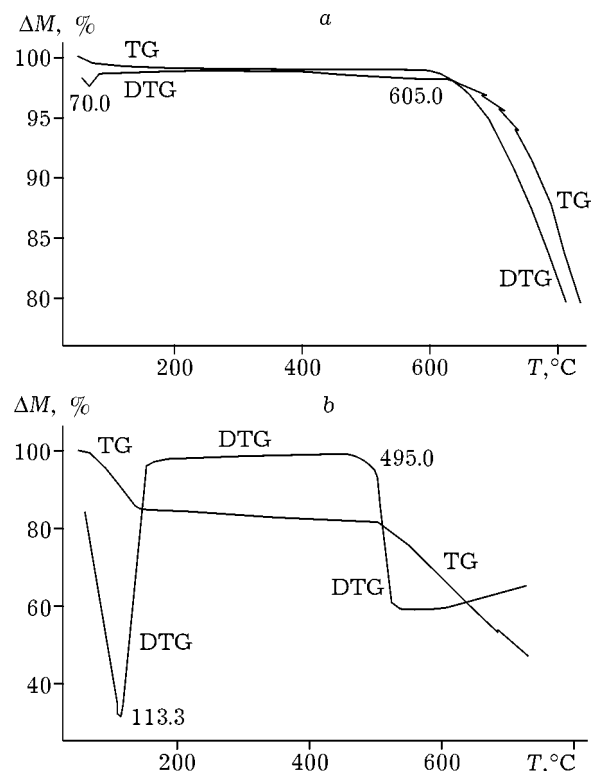


Fig. 2. Derivatograms of the CM (a) and NUMS-Sb (b).

Fig. 3. Thermograms of NUMS-O₄₀₀ (a) and NUMS-Sb₄₀₀ (b).

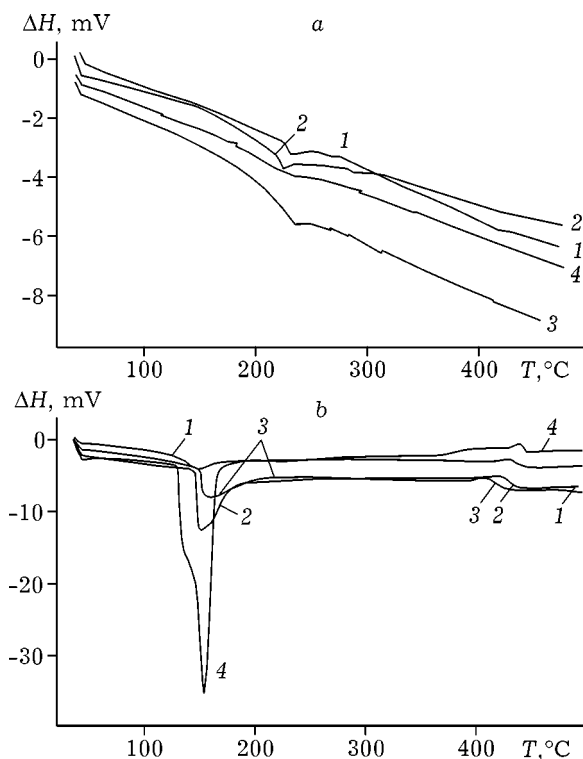


Fig. 4. Curves of enthalpy changes for NUMS-O (a) and NUMS-Sb (b) samples: 1 - initial; 2 - $T = 200$ °C; 3 - $T = 350$ °C; 4 - $T = 400$ °C.

effect at $T = 495$ °C the sample loses 17.5 % of its mass (see Table 2).

The curves of enthalpy changes (DSC) and their first time derivatives for NUMS-O and modified samples NUMS-Sb are shown in Figs. 4, 5. One can see in Fig. 4, a that the change in enthalpy for NUMS-O samples occurs within temperature range from 203.8 to 227.6 °C while for the modified NUMS-Sb samples (see Fig. 4, b) within the range from 143.8 to 171.6 °C, that is, at lower temperatures.

According to the plots and the data listed in Table 3, the samples distinguished among all the others are NUMS-O₄₀₀, which was oxidized at a temperature of 400 °C, and NUMS-Sb₄₀₀ sample which was modified from the former one (see Fig. 5). First, the change in enthalpy for NUMS-O₄₀₀ is smaller than that for the other samples; this suggests that its surface is more uniformly oxidized than the surface of other samples. Second, changes in the change in enthalpy for the sample NUMS-Sb₄₀₀ occurs in two stages: the first time derivative of the DSC curve (that is, the rate of enthalpy change) clearly exhibits superposition of the two

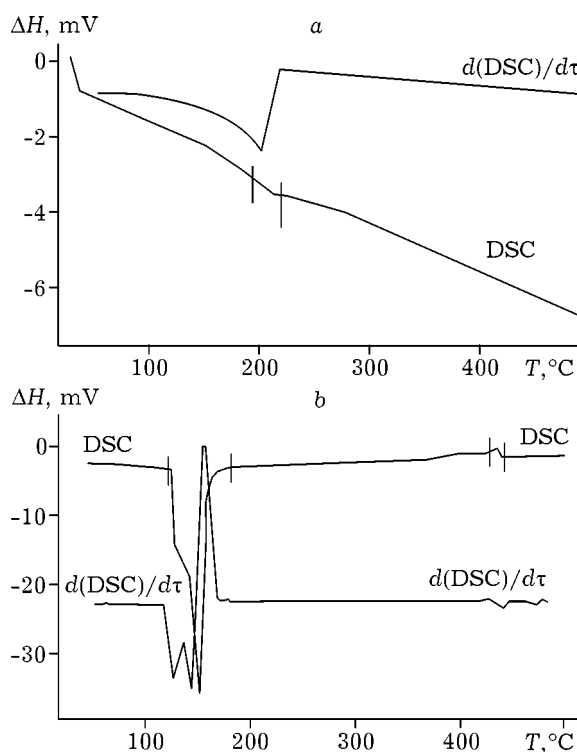
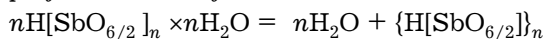


Fig. 5. Curves of changes in enthalpy and its first time derivative for NUMS-O₄₀₀ (a) and NUMS-Sb₄₀₀ (b) samples.

exoeffects; the maximum of the first one is at a temperature of 126.3 °C, the maximum of the second one is at 148 °C (see Fig. 5, b). Total enthalpy change is very large in comparison with all the other samples; it is 233.6 J/g (see Fig. 5, b). A stepwise change in the enthalpy of this sample can be explained by water removal from the hydrolyzed antimony compounds and by the formation of an intermediate stable form of crystal antimonic acid; it can also be explained by the occurrence of polycondensation of polyantimonic crystal acid:



The fact that the synthesis of polyantimonic acid was carried out on the surface of the carbon composite material due to the oxygen-containing radicals [18–20, 22] played a definite part in acceleration of water detachment process, polycondensation and formation of the polycrystalline antimonic acid on the carbon surface.

Comparing the results obtained by us with those reported previously by the authors of [23, 24] who investigated pure samples of polyantimonic acids, one may say that the

TABLE 3

Characteristics of enthalpy change DH and the maxima of temperature of exothermal and endothermic effects (T_{ex} , T_{end}) for NUMS-O and NUMS-Sb samples

T_{ox} , °C	NUMS-O		NUMS-Sb			
	T_{ex} , °C	DH , J/g	T_{ex} , °C	DH , J/g	T_{end} , °C	DH , J/g
Initial	227.8	0.9	143.8	25.8	427.7	7.0
200	219.8	1.1	145.3	49.3	419.5	2.0
250	203.8	0.6	171.6	15.9	389.6	12.7
300	205.8	1.0	163.7	11.0	379.8	2.7
350	227.6	0.8	149.6	46.6	407.5	8.1
400	211.8	0.6	148.0	233.6	435.9	3.7
450	207.7	1.4	155.8	26.9	407.7	2.9
500	207.8	1.8	165.6	35.1	383.5	1.3

polycrystalline form of antimonic acid was synthesized on the NUMS-Sb sample oxidized at $T = 400$ °C, because the foundation for the synthesis process was carbon surface, which determined the behaviour of TG and DSC curves in comparison with pure samples of polycrystalline antimonic acid.

The amorphous form of antimonic acid was synthesized on NUMS-Sb samples, initial ones and those oxidized at 200–350, 450, 500 °C, as suggested by the specific features of the carbon surface. The peaks of DSC curves have a broad, not high shape similar to the shape of DTA curves for pure amorphous form of antimonic acid. This fact can be explained by the formation of non-uniformly oxidized surface on the NUMS samples (large exothermal effects on DSC curves), that is, by the formation of a large number of oxygen-containing radicals; this hinders obtaining the crystal form of antimonic acid on the NUMS surface through oxygen bridges.

The diffraction patterns of NUMS-O samples (see Fig. 6, *a*) exhibit changes in the interplanar distances during the oxidation of the CM. The main peak of the initial CM is observed at the angle of $2\theta = 12.6$, which corresponds to the interplanar distance of 3.5310 Å. After heating the CM at $T = 200$ –350 °C, interplanar distance remains the same. Heating of the CM sample at $T = 400$ °C results in an increase in the interplanar distance to 3.589 Å, at 450 °C the interplanar distance decreases to 3.505 Å. It may be assumed that the oxidation at a temperature

of 400 °C is accompanied by the maximal saturation of the surface with oxygen, which promotes an increase in interplanar distance due to the formation of oxygen-containing radicals. This fact may have played an important part in the formation of the crystal form of antimonic acid at the NUMS-O₄₀₀ sample (see Fig. 6, *b*). The structure of graphite consists of the layers of six-membered rings; the layers are bound with each other. Together with the maximal saturation of the carbon surface with oxygen, such a structure promotes the formation of the crystal structure of antimonic acid which is based on a six-membered cell.

Heating of the CM above 400 °C causes burning-out of the carbon material and evolution is maximally oxidized carbon in the form of its oxides.

On all the other NUMS-O samples, a thin film of the amorphous antimonic acid is formed; the film repeats the relief of the surface of the carbon material (see Fig. 6, *b*, curves 1–7). The diffraction patterns of NUMS-Sb (modified on NUMS-O₂₀₀ and NUMS-O₄₀₀ samples) after heating at $T = 150$ °C are shown in Fig. 6, *b* (curves 8, 9). The X-ray phase analysis showed that after heating of NUMS-Sb the initially obtained form of the hydrolyzed antimony compound remains unchanged, that is, if the amorphous form of antimonic acid was initially obtained on the surface of CM, NUMS-O₂₀₀, NUMS-O₂₅₀, NUMS-O₄₅₀, NUMS-O₅₀₀ samples, it is conserved after heating at a temperature of 150 °C, but it undergoes polycondensation

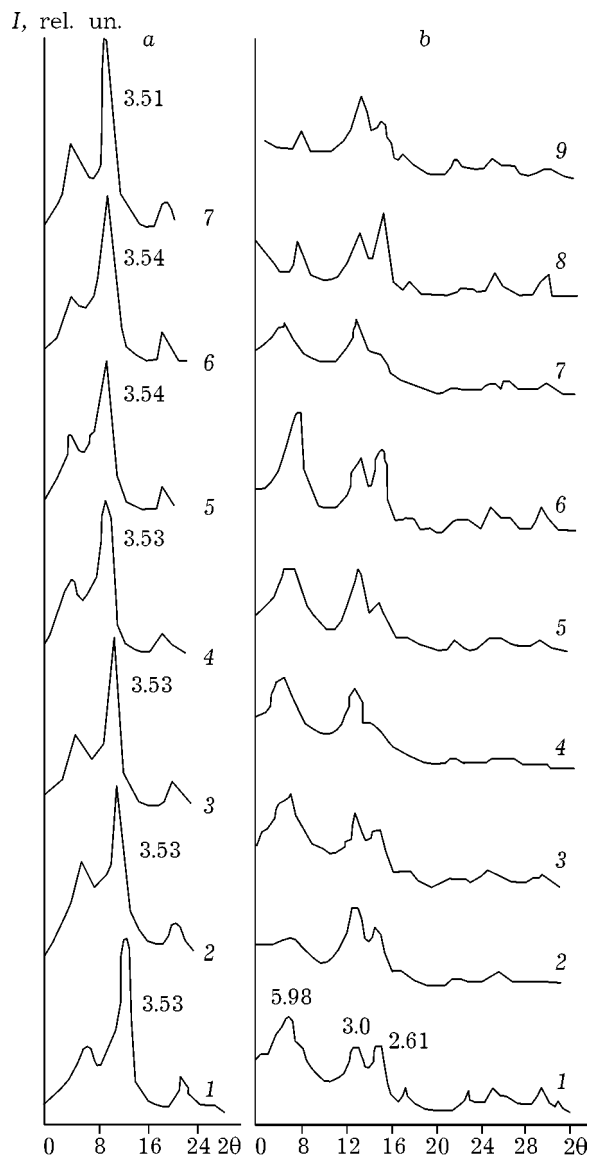


Fig. 6. Diffraction patterns of NUMS-O (a) and NUMS-Sb (b): 1 - initial; 2 - $T = 200$ °C, 3 - $T = 250$ °C, 4 - $T = 300$ °C, 5 - $T = 350$ °C, 6 - $T = 400$ °C, 7 - $T = 450$ °C, 8, 9 - NUMS-Sb after heating at $T = 150$ °C.

with water loss. The crystal antimonite was at once formed on the surface of NUMS₄₀₀; after heating to the temperature point of the first exothermal effect the crystal form of antimonite was conserved, but polycondensation took place, accompanied by water loss; $(\text{Sb}_2\text{O}_5)_n$ was formed. Comparing the results of thermogravimetric and X-ray phase analysis we may conclude that the crystal form of antimonite $\text{Sb}_2\text{O}_5 \times 3.845 \text{H}_2\text{O}$ was obtained on the NUMS-O₄₀₀ sample. It follows from the data derived from the diffraction

patterns that the pure forms, for example amorphous antimonite, can crystallize during heating or storage for a long time, while the acid forms obtained on the oxidized surface of carbon material remain unchanged (the X-ray diffraction patterns were recorded with freshly prepared samples and with the samples stored for 1.5 years).

CONCLUSIONS

1. Antimonite can be synthesized on the surface of the oxidized porous composite material (NUMS) both in the crystal form and in the amorphous one, depending on temperature of oxidation of the carbon surface.

2. The form of antimonite synthesized on the oxidized carbon surface does not change with time or during heating to 150 °C.

REFERENCES

- 1 M. Dubinin, *Z. Phys. Chem.*, 140 (1929) 81.
- 2 H. K. Kruyt, G. S. de Kadt, *Koll. Z.*, 47 (1929) 44.
- 3 R. N. Swith, J. Duffield, R. A. Pierotti, J. Mooi, *J. Phys. Chem.*, 60 (1956) 495.
- 4 U. Hofmann, G. Ohlerich, *Angew. Chem.*, 62 (1950) 16.
- 5 L. M. Levchenko, V. N. Mitkin, T. N. Denisova *et al.*, Issledovaniye protsessov izvlecheniya kaltsiya i natriya iz rastvorov litiyevykh soley na novykh tipakh modifitsirovannykh uglerodnykh sorbentov: Trydy 2-go Mezhdunar. Sem. "Uglerodnye sorbenty", Kemerovo, 2000, pp.160-163.
- 6 L. M. Levchenko, V. N. Mitkin, V. E. Kerzhentseva *et al.*, Issledovaniye nanofaznykh polimerov sur'myanoy kisloty, nanesennykh na gidrofobnye i gidrofil'nye matritsy, Trudy "Nanokhimiya: novye podkhody k sozdaniyu polimernykh sistem so spetsificheskimi svoystvami", Tashkent, 2003, pp. 123-136.
- 7 L. M. Levchenko, V. N. Mitkin, V. E. Kerzhentseva *et al.*, Novye tipy uglerodsoderzhashchikh sorbentov dlya izvlecheniya shchelochnykh i shchelochno-zemel'nykh metallov iz tekhnologicheskikh rastvorov i perspektivy ikh primeneniya dlya sorbtsii radionuklidov iz zhidkikh otkhodov, Materialy 7-y nauch.-prakt. konf. Sibirskogo khim kombinata, part 3, SGTI, Seversk, 2003, pp. 91-95.
- 8 L. M. Levchenko, V. N. Mitkin, V. E. Kerzhentseva *et al.*, Rol' koordinatsionnykh soyedineniy v protsessakh ochistki litiysoderzhashchikh rastvorov na novykh sinteticheskikh uglerodnykh sorbentakh, Mezhdunar. Chugaevskaya konf. po koordinats. khimii, Kiev, 2003, pp. 92-94.
- 9 I. V. Shemyakina, L. M. Levchenko, V. V. Mukhin, V. N. Mitkin, Protssesy kompleksobrazovaniya na ugol'noy poverkhnosti, Tez. Dokl. Mendeleevskogo s'yezda po obshchey i prikl. khimii, Kazan', 2003, p. 463.

- 10 Pat. 4929588 US, 1990; Pat. 4859343 US, 1989.
- 11 Pat. 4590175 US, 1986.
- 12 J. Lefebvre, *Compt. rend.*, 260 (1965) 5575.
- 13 M. Abe, T. Ito, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 87 (1966) 1174.
- 14 M. Abe, *J. Inorg. Nucl. Chem.*, 41 (1979) 85.
- 15 B. G. Novikov, F. A. Belinskaya, E. A. Materova, in: *Ionny obmen i ionometriya*, Izd-vo LGU, Leningrad, 1979, vol. 2, p. 21.
- 16 B. G. Novikov, F. A. Belinskaya, E. A. Materova, *Ibid.*, p. 32.
- 17 N. S. Grigorova, F. A. Belinskaya, E. A. Materova, *Ibid.*, 1976, vol. 1, p. 81.
- 18 F. A. Belinskaya, L. A. Karmanova, *Ibid.*, p. 58.
- 19 B. G. Novikov, F. A. Belinskaya, E. A. Materova, in: *Vestnik Leningradskogo un-ta*, 1969, vol. 10, p. 97.
- 20 B. G. Novikov, F. A. Belinskaya, E. A. Materova, *Ibid.*, 1976, vol. 22, p. 100.
- 21 D. V. S. Yain, A. K. Banerjee, *J. Inorg. Chem.*, 19 (1961) 177.
- 22 *Rukuvodstvo po neorganicheskomu sintezu*, in G. Brauer (Ed.), Mir, Moscow, 1985, vol. 2, pp. 632–633.
- 23 B. G. Novikov, E. A. Materova, F. A. Belinskaya, *RZhKh*, 6 (1975) 1566.
- 24 M. Abe, *Synthetic Inorganic Ion-Exchange Materials*, Institute of Technology Ookayama, Meguro-ku, Tokyo, Japan, vol. 13, No. 4, 1978, p. 347.