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MODIFICATION OF ACTIVATED CARBON KAU SURFACE PROPERTIES

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The properties of oxidized activated carbon KAU treated at different temperatures in inert atmosphere were studied by means of DTA, Boehm titration, XPS and AFM methods and their catalytic activity in H_2S oxidation was established. Three types of oxygen species exist on carbon catalysts surface. It was shown that their catalytic activity in hydrogen sulfide oxidation correlated with relative content of OH-groups and charged oxygen species on carbons surface ($O_{2.1}$ and $O_{3.1}$ oxygen types with $BE = 533.2–533.7$ and $536.8–537.6$ eV, respectively). The sample treated at 1000°C has very high activity in H_2S oxidation and transforms up to 57 mmol H_2S/g cat at 180°C. The vanadium/carbon KAU samples were prepared by three different methods (incipient wet impregnation and deposition-precipitation by NH_4VO_3 in aqueous medium, and in acetonitrile with $VO(acac)_2$). It was established that synthesis in organic medium led to preparation of nanodispersed vanadia on carbon surface. The V/C samples were more active in H_2S oxidation at 180°C than treated activated carbons. The sample prepared in organic medium had excellent activity in hydrogen sulfide oxidation and oxidized more than 132 mmol H_2S/g cat without its deactivation. The formation of surface dense sulfur layer is the reason of catalysts deactivation in H_2S selective catalytic oxidation.

INTRODUCTION

A currently important aspect of environmental policy is removal of sulfur-containing species from various gases. Toxicity of sulfur-containing compounds and their very low odor threshold determine the development of efficient desulphurization processes. Governments are constantly tightening regulations to limit the emission of sulfur compounds into air and this makes necessary to enhance the level of sulfur recovery from natural, refinery, gasification, cracking, municipal, and other gases.

The most widely used method for H_2S removal is Claus process based on reaction of selective transformation of H_2S to elemental sulfur

$$2H_2S + SO_2 = (3/n)S_n + 2H_2O.$$
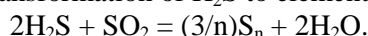
The thermodynamic limitations of the Claus equilibrium reaction fix the maximum hydrogen sulfide conversion level at about 97%. The developed Superclaus process permits to reach efficiency up to 99.5%. These processes are very effective at stable and large sources of raw material (H_2S). Their technological features, advantages and disadvantages were summarized in reviews [1, 2].

However, these processes lose their advantages and efficiency at low H_2S content (below 5%) in gas mixtures or its not-stable source. Adsorption or catalytic methods use for hydrogen sulfide removal from a tail gas and the last technology based on direct H_2S selective oxidation by air oxygen to elemental sulfur $n\,H_2S + O_2 = n/2\,S_n + H_2O$ seems more promising although the catalysts of this reaction still need to be improved.

Catalysts on the base of metal oxides (bulk or supported) proposed for direct hydrogen sulfide selective oxidation at its low concentration [3–10] and vanadium containing compositions were among the most promising catalysts. However the high activity of oxide catalysts leads to formation of SO_2 (dangerous pollutant also) and reduces the selectivity of the reaction. Sulphatation of the oxide catalysts or supports provokes decrease of their activity or destruction.

Carbon containing materials also were proposed as catalysts for the low temperature H_2S oxidation above or below the sulfur dew point [e.g., 11–19]. It was shown [e.g., 18] that nickel sulfide supported on high surface area SiC was active and selective below dew point and oxidized H_2S at low oxygen concentration ($O_2/H_2S = 2.5$)

with sulfur storage of almost 120 wt.% (1200 mg/g). This catalyst could be regenerated by sulfur removal at 250–300°C in inert gas (He). However, an increase of the reaction temperature or oxygen concentration decreased the oxidation selectivity and led to SO_2 formation. The maximal values of the sulfur storage on carbon catalysts were obtained at 200°C (690 mg/g) [11].

The unique surface properties of carbonaceous materials, such as high surface area and pore volume, along with their chemical properties and possibility of their modification make them very attractive for preparation of catalysts with better properties in direct selective H_2S oxidation at low reaction temperatures. The most common ways [e.g., 20–23] for modification of carbon surface are: impregnation with metal salts, controlled oxidation and thermal treatment of carbons materials. In this study carbon surface was activated by HNO_3 treatment as an effective method of oxygen-containing groups introduction and surface modification followed by their thermal treatment in inert atmosphere at different temperatures and by impregnation with vanadium salts.

Previous study [24] has shown that modification of carbon surface by metals (V/C, Mn/C, Fe/C, Co/C, Cu/C and Mo/C) changes its properties and increases activity in hydrogen sulphide oxidation, and that vanadium-containing sample (vanadium content near 1 wt.%) was the most promising catalyst for this process at low H_2S concentration in air. In this paper the influence of the preparation method on the properties of the V/C system was studied.

EXPERIMENTAL

Activated carbon KAU prepared from peach and apricot stones was used as raw material. It was treated during 4 h in 2M solution of NaOH at 95–100°C washed in water to bring pH of solution down to 10, treated with hot hydrochloric acid, washed with water to bring pH of solution up to 4, then carbonized at 650–700°C and activated with steam at 800–850°C (KAUin). The analysis of KAUin sample with Carlo Erba Strumentazione elemental analyzer (mod. 1106) showed the presence of C (94.3 wt.%), H (0.5 wt.%) and O (5.2 wt.%). The content of mineral admixtures was determined by ashing carbon sample in furnace at 900°C. KAUin sample contained a smaller quantity of mineral admixtures (ash content = 0.4 wt.%). The analysis of ash composition (EDXRS) showed that the base

elements were Ca and Na, and only traces of Al, Si and Fe were determined. This initial carbon was oxidized in 25% HNO_3 at 95°C during 4 h, washed with water and dried at 110°C for 4 h (KAUox). The oxidized activated carbon KAUox was calcined in argon flow at steadily increasing temperature (2°C/min) and then the samples were heated step by step in 2 h at the following temperatures: 400°C (KAU400), 600°C (KAU600), 800°C (KAU800) and 1000°C (KAU1000).

Vanadium-containing catalysts were prepared by three methods with KAUin as support: i) incipient wet impregnation in water solution with NH_4VO_3 (0.69 g of vanadium salt on 30 g of the support) (Vaq/Ciw), ii) deposition-precipitation in water solution with NH_4VO_3 (0.69 g of vanadium salt on 30 g of the support) (Vaq/Cdp), iii) support impregnation with $OV(C_5H_7O_2)_2$ (1.56 g of $VO(acac)_2$ on 30 g of the support) in acetonitrile medium (Vacac/C). The prepared samples (6 g of each sample) were dried during 6 h in air at 110°C and calcined in flow of Ar in tubular quartz reactor (Ø 25 mm and 50 cm in length) at 450°C for 4 h.

The textural characterization of the activated carbon samples was based on the N_2 adsorption isotherm determined at –196°C with a Quantachrome NOVA/2200e system. Prior to measurement, samples were outgases overnight at 120°C under nitrogen flow. The pore volumes and pore size distributions were calculated using density functional theory. Additionally, the surface areas and pore volumes were calculated using the BET and Dubinin–Radushkevich methods.

The surface groups were determined quantitatively following the Boehm titration method [25]. Thermal analysis of the samples was realized with a Derivatograph Q-1500 "F. Paulik, J. Paulik, L. Erdey" thermoanalytical instrument at heating rate 5°C/min in air atmosphere.

The amount of vanadium in the catalysts was measured by atomic absorption spectroscopy and it was practically equal to 1 wt.% in all samples.

The surface composition of the catalysts was obtained from XPS spectra recorded by a VG Scientific ESCA-3 photoelectron spectrometer using Al $K\alpha_{1,2}$ radiation (1486.6 eV). The X-ray source operated at 13 kV and 10 mA. The working pressure was lower than $2 \cdot 10^{-8}$ Torr (1 Torr = 133.3 Pa). All spectra were recorded at the photoelectron take-off angle of 45°. Binding energies were referenced to the C 1s peak at

284.8 eV from the graphitic peak (maximal intensity). The spectrometer was interfaced with an IBM PC AT microcomputer for data acquisition and processing. The data published in [26–32] were used for the correct identification of obtained results.

The surface morphology of the samples was studied by atomic force microscopy (AFM) with a NanoScope E, Digital Instruments Scanning Probe Microscope Controller.

The catalytic properties of the samples were determined in reaction of hydrogen sulfide oxidation using a flow type quartz reactor (8 mm diameter and 45 cm in length) with cool flask below reactor. The reaction was performed in temperature range 20–180ºC with the reaction mixture containing 1 vol.% H_2S in air ($O_2/H_2S = 20$). The velocity of the reaction mixture was 50 cc/min and nearly 0.5 g of the catalyst (1 cm^3) was loaded into the catalytic reactor. The content of hydrogen sulfide in the reactor inlet and outlet was controlled by GC method and the appearance of H_2S traces (20 ppm) on the catalytic reactor outlet was additionally qualitatively fixed by change of color of the filter paper moistened in 1M solution of lead acetate. For the determination of true catalytic properties of the carbon catalysts without masked influence of catalytic properties of sulfur and possible dissolution of H_2S in deposited sulfur (see above), the activity of carbons was determined as the quantity of oxidized hydrogen sulfide up to first appearance of H_2S traces in catalytic reactor outlet.

RESULTS AND DISCUSSION

DTA method shows that KAUin activated carbon sample is stable to oxidation by air up to temperatures of 480–500°C (Fig. 1). Oxidation of this activated carbon by HNO_3 leads to the decrease of its thermal stability – the surface oxidation of KAUox begins at temperature of 100–120°C and burning is observed at 180–200°C. Calcination of KAUox in inert atmosphere independently on the treatment temperature increases the thermal stability of the samples. Data presented in Fig. 1 show that the temperature of mass loss beginning for the samples KAU600-KAU1000 is not so much different from the value for KAUinit activated carbon. The deposition of vanadium on carbon KAUin surface also increases its temperature of oxidation beginning up to 300°C for Vaq/C samples and up to 350°C for Vacac/C

catalyst. These results demonstrate the stability of the synthesized samples under the reaction conditions used for hydrogen sulfide oxidation.
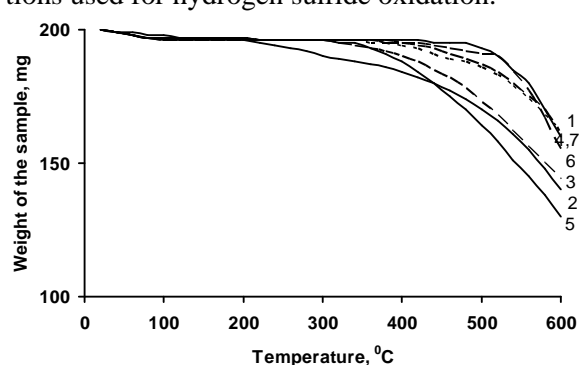
Fig. 1. Thermogravimetric data of activated carbons oxidation by air; *1* – KAUinit, *2* – KAUox, *3* – KAU600, *4* – KAU1000, *5* – Vaq/Ciw, *6* – Vaq/Cdp, *7* – Vacac/C)

The characteristic isotherms of nitrogen adsorption obtained on studied samples are presented in Fig.2.
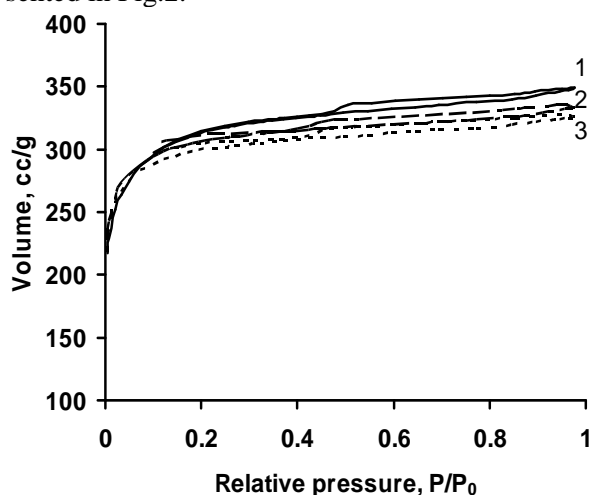
Fig. 2. The isotherms of nitrogen adsorption on KAUox (*1*) and V/C samples: Vacac/C (*2*), Vaq/Ciw (*3*)

The presence of type H4 (E in old classification) of the hysteresis loop on the isotherms shows the existence of some mesoporosity in the samples. The curves of adsorption and desorption are practically horizontal and parallel in wide range of relative pressures that can indicate the preferential microporosity of prepared materials with slit-shaped pores. The deposition of vanadium on carbon surface leads to the shift of the isotherm downward.

The textural parameters of the preparations calculated from the isotherms of nitrogen adsorption are presented in Table 1. The obtained results show that for all samples the specific surface area

and micropore volume have the practically identical values. Thus the modification of KAUox sample by high temperature treatment in an inert atmosphere and KAUin by vanadium deposition less influences on this parameters of the sample porous structure.

Table 1. Textural parameters of the samples calculated from nitrogen adsorption at -196ºC*

Sample	S_{BET}, $m^2 \cdot g^{-1}$	V_{tot}, $cm^3 \cdot g^{-1}$	V_{mic}, $cm^3 \cdot g^{-1}$	R, nm	E_0, $kJ \cdot mol^{-1}$	S_{ex}, $m^2 \cdot g^{-1}$	S_{mic}, $m^2 \cdot g^{-1}$
KAUin	1240	0.55	0.52	0.88	–	20.1	1042
KAUox	1150	0.54	0.51	0.94	7.65	4.8	1100
Vaq/Ciw	1140	0.51	0.48	0.89	9.16	1.7	1126
Vaq/Cdp	1130	0.50	0.47	n.d.	9.12	12.6	0.45
Vacac/C	1170	0.54	0.52	0.89	8.97	15.0	1065

*S – specific surface area by BET method, V_{mic} and E_0 – micropore volume and the characteristic adsorption energy calculated by DR method, R – average pore width determined by Dubinin method, V_{tot} – cumulative pore volume determined from pores size distribution.

The distribution of the pores for KAUin sample demonstrates two maxima at the pore radius equal to 2.4 and 7.0 Å (Fig. 3).
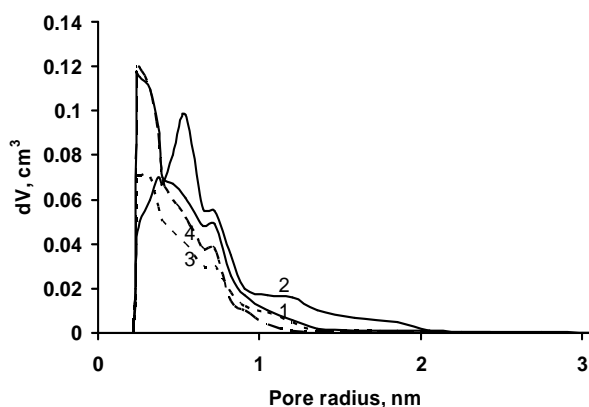
Fig. 3. Pore distribution of sizes for the KAUinit (*1*), KAUox (*2*) and V/C samples: Vaq/Ciw (*3*), Vacac/C (*4*)

Deposition of vanadium on KAUin from water and organic solutions results in formation of samples with different properties. Pore size distribution for a sample synthesized in non-aqueous environment practically completely coincides with initial activated carbon. It testifies that VO(acac)$_2$ does not penetrate in micropores and, most likely, concentrates on an external surface of the carbon support. This assumption may be confirmed by V/C atomic ratio calculated from XPS data (Table 4). Vanadium concentration on

surface of Vacac/C sample is three times higher than in Vaq/Ciw sample. The porous structure of the sample Vaq/Ciw well corresponds to those of the support up to pore sizes of 6 Å but the difference observes in micro- and mesoporous regions. This fact can be connected with the penetration of ammonium vanadate in the big radius pores only. These data show that the vanadium deposits on the walls of wide micro- and mesopores of carbon support and partially fill up them.

The results of Boehm titration presented in Table 2 suggest that all carbon samples possess acid (i.e., carboxylic, lactonic and phenolic groups) and basic functional groups. The amount of both groups and especially strongly acid groups (i.e., carboxylic groups) increased after KAUin sample oxidation. Lactonic groups are prevalent among acid sites on the KAUox sample but their content essentially decreased with an increase of the calcination temperature in inert atmosphere.

Table 2. The concentration of surface functional groups in carbons determined by Boehm titration

Sample	pH	Content of surface groups, meq/g				
		carbo-xylic	lactonic	phenolic	total acidic	total basic
KAUinit	5.74	0.066	0.38	0.95	1.40	0.3
KAUox	3.78	0.526	1.48	0.49	2.50	1.2
KAU400	5.75	0.432	1.12	0.43	1.98	1.1
KAU600	6.62	0.232	0.37	0.36	0.96	1.0
KAU800	7.78	0.014	0.23	0.15	0.39	0.6
KAU1000	8.88	–	0.06	0.01	0.07	0.3

The data in Table 2 show that the concentration of the acid groups more decreases than that of the basic ones and it is accompanied by an increase of the pH of the carbon suspension. After the sample treatment at 1000°C, the residual amount of surface acid groups was below the detection limit of the Boehm titration. This result could be attributed to the higher thermal stability of the basic surface groups compared to acid ones. This corresponds to literature data [33] which show that in lower temperature range (120–500ºC) strong acid groups (carboxylic groups) decompose easily than weak acids groups (phenols and lactonic) and oxygen-containing organic bases (500–800ºC).

The XPS study of the surface in prepared activated carbons show the some asymmetry of C 1s peak. According to literature [26–32], the carbon

spectra were well fitted with five peaks which were assigned to carbon atoms bound with carbon and/or hydrogen atoms (BE = 284.8 eV, $C_{1.1}$ peak), to carbon atoms with one ($C_{2.1}$), two ($C_{3.1}$) and three ($C_{4.1}$) bonds with oxygen atoms (BE = 286.2–286.3, 287.7–288.1 and 289.2–290.4 eV, respectively) and to π–π*peak ($C_{5.1}$, BE = 291.2–291.8 eV). The treatment of activated carbon not much influenced the electronic state of carbon atoms and C1s binding energies. The oxidation of KAUinit sample slightly decreased the intensity of $C_{1.1}$ (the main peak – 60–70% relative intensity of C 1s peak) and $C_{5.1}$ peaks and increased the area of the peaks assigned to carbon-oxygen groups but the thermal treatment of KAUox carbon in inert atmosphere reduced the content of oxygen containing groups ($C_{2.1}$–$C_{4.1}$).

The O 1s spectra of studied carbons were fitted with three peaks and their binding energies are reported in Table 3.

Table 3. The binding energy of O 1s-electrons and relative content of O1s peaks (XPS method) on samples surface

| Sample*	BE of O 1s-electrons, eV			Area of O1s peak, %		
	$O_{1.1}$	$O_{2.1}$	$O_{3.1}$	$O_{1.1}$	$O_{2.1}$	$O_{3.1}$
KAUinit	530.6	533.4	537.1	26.7	58.2	15.1
KAUox	530.6	533.3	536.9	43.8	49.6	6.6
KAU400	531.0	533.7	536.9	41.4	50.0	8.6
KAU600	530.9	533.7	536.8	38.2	50.9	10.9
KAU800	530.8	533.6	537.1	31.5	51.8	16.7
KAU1000	530.4	533.5	537.6	24.3	54.9	20.8
Vaq/Ciw-bc	530.8	533.2	537.5	33.6	56.3	10.1
Vaq/Cdp-bc	530.5	533.6	537.3	34.1	57.2	8.7
Vacac/C-bc	530.1	532.8	536.4	35.5	58.1	6.4
Vaq/Ciw-ac	531.4	533.0	537.1	47.4	47.8	4.8
Vaq/Cdp-ac	531.3	533.2	537.0	49.3	46.7	4.0
Vacac/C-ac	531.6	533.3	537.1	59.6	38.2	2.2

* V/C-bc and V/C-ac – the catalysts before and after catalytic tests, respectivelly

In agreement with literature [26–29, 31–32] the $O_{1.1}$ peak with BE 530.4–531.0 eV was assigned to C=O type oxygen (C=O, COOR). The second peak $O_{2.1}$ (BE 533.2–533.8 eV) corresponds to C–O type oxygen in C–OH and COOR groups. Three assignments are possible for the $O_{3.1}$ peak with BE 536.8–537.7 eV. According to published data, it may be due to adsorbed water or oxygen [26, 28, 32], "charged" oxygen species [29] or a shake-up peak [27]. The BE near to 539 eV is characteristic for shake-up peak [27]. On other hand, the binding energy of O

1s-electrons of adsorbed water were determined in the range 535.0–536.0 eV while for adsorbed oxygen BE = 537.3–537.6 eV were observed [28, 32]. Therefore, the $O_{3.1}$ peak may be assigned to oxygen adsorbed on carbon surface. Taking into account the possible transfer of π electrons density from carbon at sorption of hetero-atoms [34], this oxygen can have an excess of electron density. The formation of adsorbed superoxide O_2^- on carbon surface with BE > 536.0 eV was supposed in [35] and in [20] was proposed that π electrons of carbon could activate oxygen to O_2^{2-} species which dissociate to O^- species.

The relative content of different oxygen species (see Table 3) shows that oxidation of KAUinit with HNO_3 increases the $O_{1.1}$ peak area and decreases the area of $O_{2.1}$ and $O_{3.1}$ peaks. This corresponds to the increase of the amount of carboxylic and lactonic groups and to the decrease of the content of phenolic groups (determined by Boehm titration – see Table 2). After treating KAUox in inert atmosphere, the relative content of $O_{1.1}$ oxygen decreased while the amount of $O_{2.1}$ and $O_{3.1}$ species increased (Table 3). The decrease of relative intensity of the $O_{1.1}$ peak corresponds to the moving off of the quantity of carboxylic and lactonic groups (Table 2) and their relative content. The treatment of the sample in an inert gas at high temperatures led to formation of unsaturated defects at carbon surface [34]. They can adsorb oxygen with charge transfer causing the increase of $O_{3.1}$ peak intensity (Table 3).

The data presented in Fig. 4 demonstrate an approximately linear correlation between the amounts of oxygen containing groups (acid groups) determined by Boehm titration and the sum of areas of $O_{1.1}$ and $O_{2.1}$ XPS peaks.
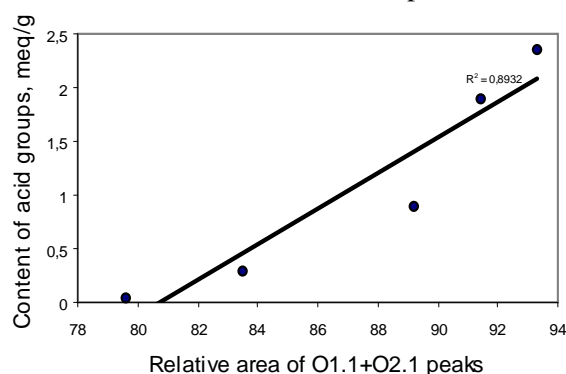
Fig. 4. The content of acid groups on activated carbons determined by Boehm titration *vs* the relative area of oxygen containing functional groups ($O_{1.1}$+$O_{2.1}$) from XPS spectra

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These results show that XPS data quite well describe the chemical changes at the surface of treated activated carbons.

The catalytic activity of the activated carbon samples in hydrogen sulphide oxidation was defined (see Experimental) as quantity of H_2S transformed (with conversion equal to 100%) until the first appearance of hydrogen sulfide (20 ppm) in the outlet of reactor. The data obtained (Fig. 5) show that the reaction temperature strongly influenced the catalytic activity of the carbons.
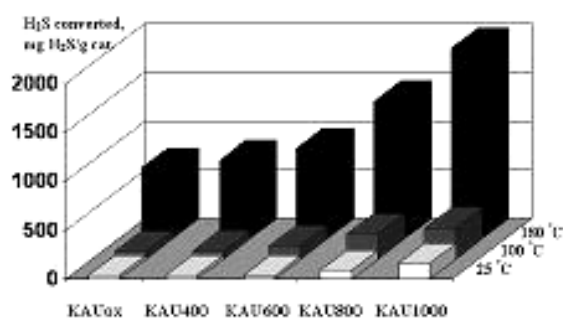

Fig. 5. The catalytic activity of activated carbons in oxidation of hydrogen sulfide at different reaction temperatures

Low activity in H_2S oxidation at 25°C was observed for all samples but the treatment in an inert atmosphere at temperature more than 800°C little increased the quantity of H_2S oxidized. The more active catalyst KAU1000 oxidizes 160 mg H_2S/g at 25°C. The increase of reaction temperature up to 100°C slightly influenced the catalytic activity of the samples. The catalytic activity of the carbons considerably increased at 180°C. On the other hand, the activity of the samples increased with increasing temperature of the carbons treatment in inert gas (Fig. 5) and KAU1000 at 180°C oxidized 1980 mg H_2S/g of catalyst. This quantity is more than two times higher that described in literature [12].

The analysis of the gas mixture composition in the outlet of the reactor did not show the presence of SO_2. The XPS study of the carbons KAU after catalytic tests showed the presence of one peak only in the S 2p spectra at 164.0–164.3 eV which is characteristic of elemental sulfur [36]. Absence of SO_x in the reaction products and on the catalysts surface shows that the reaction of H_2S oxidation under our conditions selectively proceeds to the formation of elemental sulfur. Quantity of sulfur formed from the H_2S oxidation at 25°C on KAU1000 catalysts (150 mg Sx/g) is

insufficient to fill fully the volume of pores (at amorphous sulfur density 1.92 g/cm^3 [37] near 20% of volume is filled up) or to form the monolayer (amount of sulfur is near 3 atom/nm^2) but this amount is capable to cover and deactivate the surface active centers of the catalyst. Increase of the reaction temperature up to 180°C gives more sulfur (1980 mg/g for KAU1000) which quantity is sufficient to fill pores and cover surface with more than monolayer (34 atom S/nm^2). At this temperature the sulfur partial pressure [37] is not high enough and only a part of the formed sulfur desorbs and condensates on cool walls and flask below the reactor. However, most sulfur remains on the catalyst surface and deactivates its.

The results obtained by us and the data published in literature [38–41] allow to suggest that hydrogen sulfide oxidation proceeds *via* dissociative adsorption of H_2S with participation of surface OH-groups ($O_{2.1}$ type) and/or charged oxygen species ($O_{3.1}$ type). This conclusion agrees with the data for KAU carbon catalysts in Fig. 6 which shows a good linear correlation between the amount of hydrogen sulfide oxidized at 100°C ($R^2 = 0.97$) and 180°C ($R^2 = 0.93$) and the relative content of $O_{3.1}$ oxygen species or $O_{2.1}$ oxygen type ($R^2 = 0.95$ and $R^2 = 0.91$ at 100 and 180°C, respectively).
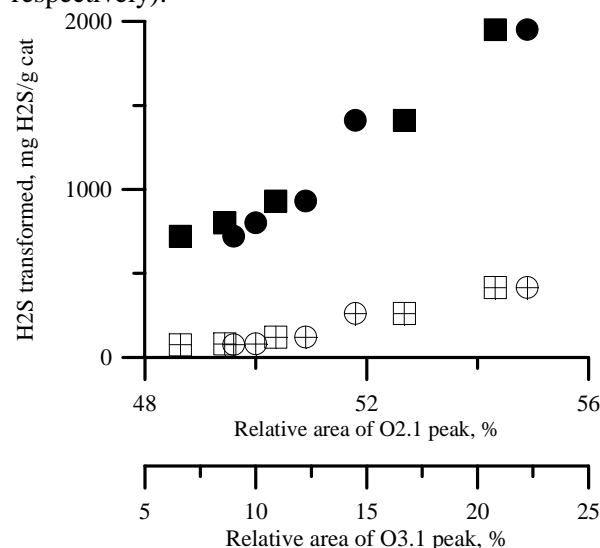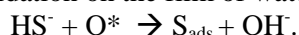

Fig. 6. The amount of oxidized hydrogen sulfide at 100°C (⊠ ○) and 180°C (■ ●) *vs* relative content of $O_{2.1}$ type (⊠ ■) or $O_{3.1}$ type (○ ●) of oxygen on carbon catalysts surface

Therefore, we can conclude that hydrogen sulfide dissociation on carbon surface can proceed via following schemes
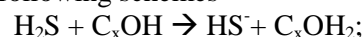
$$H_2S + C_xOH \rightarrow HS^- + C_xOH_2;$$

$$H_2S + C_xO^{\sigma-} \rightarrow HS^- + C_xOH \text{ or } S^{2-} + C_xOH_2$$

and next oxidation on the film of water

$$HS^- + O^* \rightarrow S_{ads} + OH^-.$$

These reactions lead to formation of hydroxyl group or adsorbed water and HS^- or S^{2-} ions. The last species can transfer electron(s) to the carbon surface becoming HS° or S° radicals. It is known that two HS° or S° radicals can recombine to S_2 [42] quickly transformed to S_x [43].

Vanadium deposition on KAU surface less influences on the shape of O 1s band (Fig. 7) and the binding energies of the component oxygen species (Table 3). However, independently on preparation method the peak area of $O_{1.1}$ species increases while the relative content of $O_{2.1}$ stay unchangeable and $O_{3.1}$ oxygen types decreases. These results can give evidence that oxygen of the vanadium deposited has the same nature, as C=O type of carbon support oxygen. Stability of $O_{2.1}$ peak area testifies that this form of oxygen does not participate during deposition of vanadium precursor on a carbon surface. The decreases of relative content of $O_{3.1}$ peak in two-three times in comparison with initial carbon KAU suggest that vanadium oxides can be formed on oxygen chemisorption places.

The binding energy of V $2p_{3/2}$-electrons is 517.4 eV for all samples independently on the method of their preparation (Table 4).

Table 4. Surface properties of V/C catalysts before and after catalytic tests determined by XPS method

| Sample*	Binding energy, eV		Relative content of elements, %				Atomic V/C ratio
	V 2p	S 2p	C	O	V	S	
KAUox-bc	–	–	84.0	16.0	–	–	–
KAUox-ac	–	164.2	84.6	14.3	–	1.1	–
Vaq/Ciw-bc	517.4	–	92.4	7.2	0.4	–	0.004
Vaq/Cdp-bc	517.3	–	91.5	8.0	0.5	–	0.005
Vacac/C-bc	517.4	–	89.3	9.4	1.3	–	0.014
Vaq/Ciw-ac	517.4	164.3; 169.0	81.7	16.0	0.7	1.6	0.008
Vaq/Cdp-ac	517.4	164.5; 169.1	81.4	16.1	0.7	1.8	0.009
Vacac/C-ac	517.3	164.6; 169.1	80.4	16.2	0.3	3.1	0.004

* V/C-bc and V/C-ac – the catalysts before and after catalytic tests, respectivelly

This value points to the presence on carbon surface of both V^{5+} and V^{4+} ions. It is also important to note that the surface concentration of vanadium for sample prepared in organic medium (Vacac/C) is three times greater than that in the case of aqueous preparation used. This fact can be connected with the different size of initial vanadium species in precursor solutions that leads to difference in structure of vanadium species deposited at carbon surface from organic medium and from water.


a

b

c
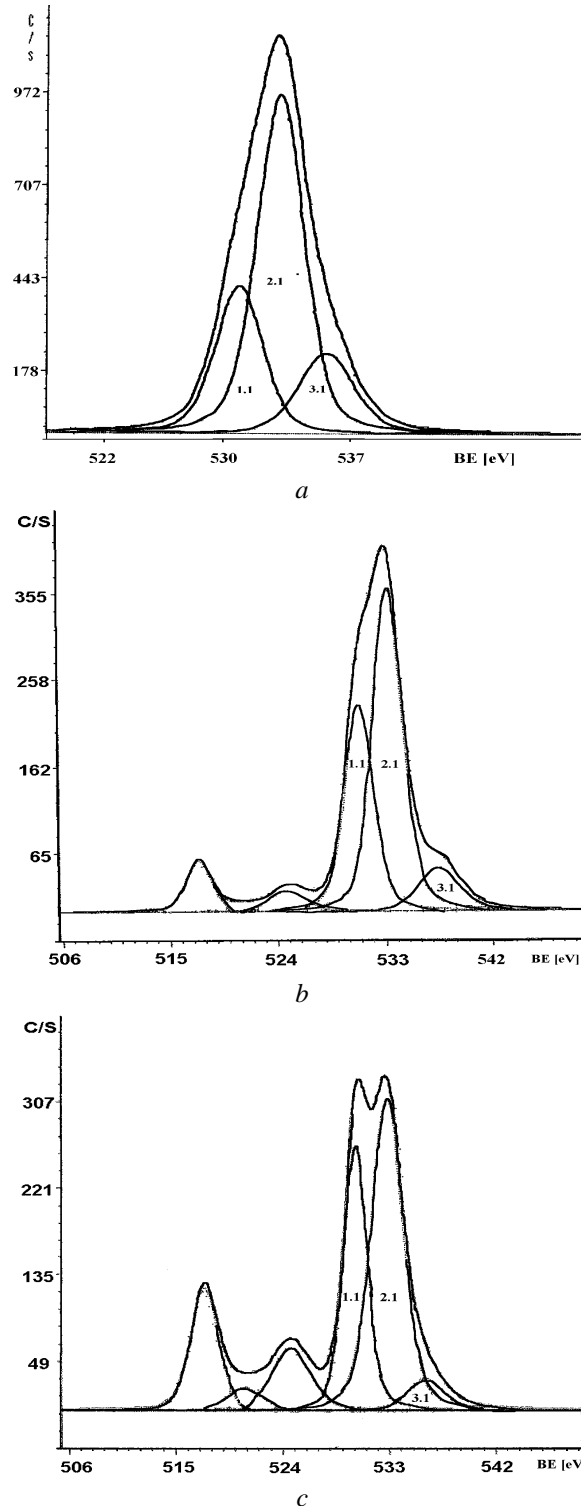
Fig. 7. The O 1s spectra (XPS) of activated carbon KAU and V/C catalysts: *a* – KAUox , *b* – Vaq/Ciw, *c* – Vacac/C

a

b

c

d

e
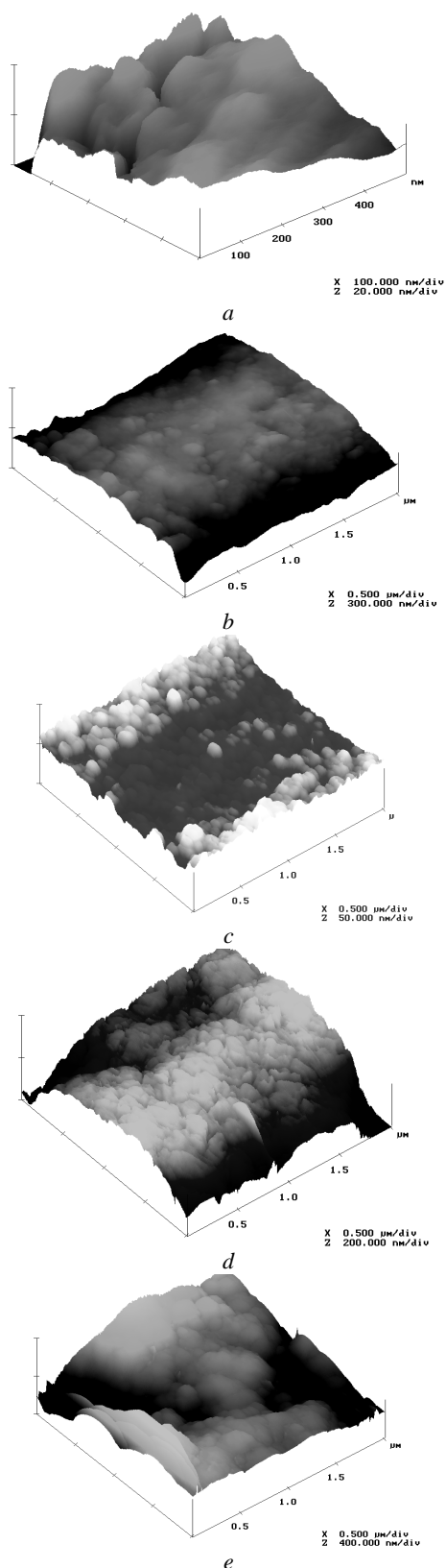
Fig. 8. The morphology of V/C catalysts surface (AFM): *a* – KAUox, *b* – Vaq/Cdp-bc, *c* – Vacac/C-bc, *d* – Vaq/Cdp-ac (after 22 h of operation), *e* – Vacac/C-ac (after 50 h of tests)

The AFM data confirmed this assumption. It is necessary to note that amount of deposited vanadium (1 wt.%) is 0.1 at.V/nm^2 being not sufficient to cover the support surface with monolayer. As Fig. 8 shows, deposition of vanadium from aqueous medium leads to the formation on carbon surface of thin layer of vanadia islands. When organic vanadium compound and organic medium were used in the synthesis, nanosized vanadia particles were obtained (Fig. 8c). The direct AFM measurement shows that these particles have the diameter near 80–100 nm and the height of 8–10 nm.

Catalytic properties of the V/C catalysts in hydrogen sulfide oxidation present Fig. 9. As it is seen the deposition of vanadium on activated carbon KAUox less influenced the catalytic activity at low temperature. Under these conditions, the amount of H$_2$S transformed on V/C samples is lower than in the case of KAU1000 catalyst. At 25°C the activity of V/C samples corresponds to KAU1000 activity that indicates absence of vanadium catalytic activity at this temperature.
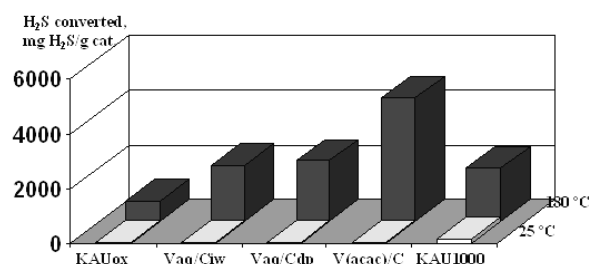
Fig. 9. The catalytic activity of V/C catalysts in oxidation of hydrogen sulfide as compared with activity of activated carbons at different reaction temperature

At higher temperature of reaction (180°C) the activity of V/C catalysts exceeds that one obtained on other KAU carbon samples. Excellent catalytic properties were demonstrated by Vacac/C catalyst (see Fig. 9) which transformed more than 4500 mg H$_2$S/g cat. without the catalyst deactivation (catalytic tests were stopped after 50 h of continuous work). This result essentially exceeds the data obtained on Vaq/C catalysts prepared in aqueous medium and other V-containing catalysts prepared by traditional methods [44]. It worth to note that obtained results gives no ground to full explanation of the vanadium-carbon catalysts activity in hydrogen sulfide oxidation.

The AFM study of V/C catalysts surface after catalytic tests shows (Fig. 8*d,e*) formation of an elemental sulfur layer on it. It covers the surface of samples prepared by traditional method in aqueous medium (Vaq/C) and it can be the reason of its deactivation in H_2S oxidation. In the case of Vacac/C sample the formation of sulfur also was observed but a part of the surface with vanadium nanoparticles remained free. These uncovered vanadium particles probable still were active in hydrogen sulfide oxidation.

The XPS study of V/C samples shows (Table 4) that after catalytic tests the binding energy of V 2p-electrons did not differ from that one in the initial samples (oxidation state of vanadium remained unchanged). The surface vanadium content after catalytic tests in the Vaq/C samples slightly increased but it decreased by four times in the Vacac/C catalyst. Simultaneously, the increase of surface oxygen content in relation to activated carbon after catalytic tests for all V/C samples was observed independently on the method of V/C catalyst preparation. Also the shift of binding energy of O 1s-electrons toward higher values for the main peak $O_{1.1}$ type species was established (Table 3) and it was practically the same in all preparations. After catalytic tests the $O_{1.1}$ peak relative area increased and that ones of $O_{2.1}$ and $O_{3.1}$ decreased (Table 3). However, these results did not permit to determine the reason of the high activity of Vacac/C catalyst in hydrogen sulfide oxidation at 180°C.

In the products of H_2S catalytic oxidation on V/C samples (up to the catalyst deactivation) only elemental sulfur and water were determined. The absence of SO_2 was verified by chromatographic analysis and $Ba(OH)_2$ test during catalytic run.

In the same time for all V/C catalysts after catalytic tests at 180°C the presence of two XPS peaks in the S 2p-band was found (Table 4). The first peak at 164.3–164.6 eV is due to elemental sulfur S^0 while the second one at 169.0–169.1 eV connected with presence of S^{6+} ions [36]. This facts can be suggested that $=SO_2$ species are strongly bonded with the V/C catalysts carbon surface and did not desorbed at these conditions, as can be expected for high heat of SO_x absorption (>80 kJ·mol^{-1}) [45].

Thus, the modification of activated carbon surface by vanadium deposition from organic vanadium compound in organic medium leads to formation of nanosized vanadium on carbon surface which has excellent catalytic activity and high stability in the hydrogen sulfide oxidation. All samples of activated carbon modified by vanadium contain increased amount of surface oxygen (Table 4) but Vacac/C sample has the maximal content of the main oxygen peak $O_{1.1}$ (Table 3) which can be connected with the formation of –V–O species highly reactive in oxidation analogous to the case of mechanochemical activated V_2O_5 [46, 47].

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Модифікація властивостей поверхні активованого вугілля КАУ

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Методами ДТА, РФЕС, АСМ та титрування за Бьомом вивчені властивості окисленого активованого вугілля КАУ, термічно модифікованого при різних температурах в інертному середовищі. Каталітична активність синтезованих зразків досліджена в реакції окиснення H_2S. На поверхні активованого вугілля встановлено присутність трьох типів кисневмісних частинок. Показано, що каталітична активність зразків в окисненні сірководню корелює з відносним вмістом ОН-груп та заряджених форм кисню на поверхні вугілля ($O_{2.1}$ та $O_{3.1}$ тип кисню з $E_{зв.} = 533,2\text{-}533,7$ та $536,8\text{-}537,6$ еВ, відповідно). Найактивніший зразок, модифікований при температурі 1000ºС, перетворив 57 ммоль H2S/г каталізатора при температурі реакції 180ºС. Зразки V/КАУ синтезовані трьома різними методами (просоченням по вологоємкості та осадженням з водного розчину NH_4VO_3, а також взаємодією с $VO(acac)_2$ в середовищі ацетонітрилу). Було встановлено, що синтез в органічному середовищі спричиняє утворення нанодисперсних кластерів ванадію на поверхні активного вугілля. Зразки, які містять ванадій, більш активні в порівнянні з термічно модифікованим вугіллям в реакції окиснення H_2S при температурі 180ºС. Зразок, синтезований в органічному середовищі, найактивніший в реакції окиснення сірководню, перетворив більш ніж 132 ммоль H_2S/г каталізатора без втрати активності. Покриття поверхні щільним шаром сірки, яка утворюється в результаті реакції, є причиною дезактивації каталізаторів в реакції селективного окиснення H_2S.

Модификация свойств поверхности активированного угля КАУ

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Методами ДТА, РФЭС, АСМ и титрования по Бёму изучены свойства окисленного активированного угля КАУ, термически модифицированного при различных температурах в инертной атмосфере. Каталитическая активность синтезированных образцов исследована в реакции окисления сероводорода. На поверхности активированного угля установлено присутствие трех типов кислородсодержащих частиц. Показано, что каталитическая активность образцов в окислении сероводорода коррелирует с относительным содержанием ОН-групп и заряженных форм кислорода на поверхности угля ($O_{2.1}$ и $O_{3.1}$ тип кислорода с $E_{св.} = 533,2\text{-}533,7$ и $536,8\text{–}537,6$ эВ, соответственно). Наиболее активный образец, модифицированный при температуре 1000ºС, окислил (превратил) 57 ммоль H_2S/г катализатора при температуре реакции 180ºС. Образцы V/КАУ синтезированы тремя различными методами (пропиткой по влагоемкости и осаждением из водного раствора NH_4VO_3, а также взаимодействием с $VO(acac)_2$ в растворе ацетонитрила). Было установлено, что синтез в органической среде обуславливает образование нанодисперсных кластеров ванадия на поверхности активного угля. Ванадийсодержащие образцы в реакции окисления H_2S при температуре 180ºС более активны в сравнении с термически модифицированным углем. Образец, синтезированный в органической среде, показал высокую активность в реакции окисления сероводорода, превратив более 132 ммоль H_2S/г катализатора без его дезактивации. Покрытие поверхности сплошным слоем образовавшейся серы является причиной дезактивации катализаторов в реакции селективного окисления H_2S.