

## Overcarbonised Adsorptive – Catalytic Systems

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### Abstract

With the use of the electron microscopy and X-ray analysis the regularities of carbon sediments formation at methane and propane pyrolysis on zeolites, Kazakhstan natural clays, chrome and bauxite sludges, which contain metal oxides of iron subgroup, have been studied. The kinetic parameters of carbon formation at methane decomposition on the surface of zeolite – CoO mixture were investigated by method of thermogravimetric analysis. The morphology and structure of forming carbon fibrils, with the metal particles fixed at their ends, have been investigated, and the formation of carbon fibrils branched pattern, so called octopus, has been discovered. Greek walnut shells and grape seeds carbonization, their immobilization by the cells of selective absorption of heavy metal and sulfur dioxide ions have been also studied. The examples of metal-carbon composites using as adsorbents for wastewater purification, C<sub>3</sub>- C<sub>4</sub> hydrocarbon cracking catalysts and refractory materials with improved properties have been considered.

### Introduction

Carbon sediments formation on catalysts while hydrocarbon raw material processing decreases catalyst activity and selectivity and, naturally, chemical reaction effectiveness. That is why a large number of works was aimed at the prevention of catalyst coking. The results are presented in R. A. Buyanov monograph [1] In one of the first works of Tesner P. A. and Rafalkes I.S. (1952) [2], devoted to the study of a carbon formation at the catalyst surface while thermal decomposition of hydrocarbons, it is pointed out that “the thermal decomposition of hydrocarbons is accompanied by a solid carbon formation, i.e. it is the process of a new solid phase origin, and it is impossible to understand it without carbon formation process careful studying”. A number of reviews have been devoted to inherent tendencies and mechanism of carbon fibril formation. Carbon sediment formation is carried out by carbide mechanism, offered by Buyanov R.A [2]. According to this mechanism, material reduction, which in its turn interacting with hydrocarbons form carbides, takes place when hydrocarbons interact with oxides. Decomposition of carbides causes the formation of iron and free carbon, on base of which carbon sediments of different structure can form.

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Carbon monoxide, hydrocarbon gases and liquids are the raw material for catalytic carbon obtaining, while metal oxides, sludge and clays are as catalysts-carries. Overcarbonization was held by dint of flow reactor in carbon pyrolysis process on salt or metal oxides of transition elements surface (pyrolysis is held under temperature conditions from 400 to 1100 °C).

As a result of pyrolysis catalytic carbon with increased specific surface, which exceed original sizes in five or ten times, forms on the catalyst surface. It is connected with morphology of carbon sediments, being fibril, tube formation and clusters with diameter of 1500–3000 Å. Besides, there are dissemination of metallic particles with diameter of 200-800 Å. It is necessary to point out that carbon fibril formation has complicated and sometimes branched structure shown in the fact that one metallic particle initiates several carbon fibril formations in different directions, so-called ‘octopus’ effect [3,5].

Recently experts on carbon materials pay attention to the process of catalytic cracking of hydrocarbons. It has been determined that Fe, Ni, Co, their oxides and also alloys of these metals are the most effective catalysts. As a result of catalytic reaction carbonaceous sediments formation is observed on dispersive metallic particles. These sediments have specific shapes and properties which allow to consider them as perspective ultradispersive systems, used in

different fields in chemistry. Over several last years certain experimental material had been gathered, which shows the development of metal-carbon composites application as adsorbents, catalyst-carriers and catalysts of the number of chemical reactions [6-10].

In present time, works connected with obtaining of overcarbonized materials on the base of local clays and mining industry waste that is chrome and bauxite sludge, agricultural wastes (walnut shells and grape kernels) and their application are held in Kaz SNU Combustion Problems Institute and Chemical Physics Department laboratories. These adsorptive-catalytic systems are used for oil purification from sulfur-bearing compounds, water purification from organic compounds and heavy metal ions, air purification from  $\text{SO}_2$  and for improved types of refractory materials production, which are used as catalyst carriers and hydrocarbons conversion reaction catalysts. The data on synthesis and studying of such systems, obtained by the author and colleagues, are given below.

## Experimental

### *Substances and overcarbonized samples preparation*

Overcarbonization of chrome sludge was held in flown conditions in quartz reactor ( $d = 30$  mm) by propane-butane mixture (60% + 40%).

A pounded fraction ( $a = 0,25-0,5$  mm), which was batchly (30g) charged in reactor, was used for the experiment.

The process was held at temperatures  $T = 500-800$  °C, times of contact  $t = 20-80$  min, gas flow rates  $3-7$  hour<sup>-1</sup>. Carbon content of overcarbonized samples was estimated by a sample combustion with a mass 1-2 g in a horizontal tube furnace in a ceramic boat at the temperature  $T = 800$  °C for 40 minutes. Percentage of carbon content was estimated by sample mass differences before and after combustion.

Natural zeolite of Altyn-Amel deposit in Kazakhstan has an averaged composition (%):  $\text{SiO}_2$  47.9;  $\text{TiO}_2$  0.84;  $\text{Al}_2\text{O}_3$  17.6;  $\text{Fe}_2\text{O}_3$  0.6;  $\text{FeO}$  0.6;  $\text{MnO}$  0.12;  $\text{CaO}$  7.3;  $\text{MgO}$  4.7;  $\text{Na}_2\text{O}$  2.6;  $\text{K}_2\text{O}$  0.5 ;  $\text{P}_2\text{O}_5$  0.1;  $\text{SO}_3$  0.1.

Zeolite was granulated in laboratory conditions, where China clay was added as a binding. Cobalt oxide (11) was added by mechanical mixing with beforehand grinded zeolite (0.5 mm). Concentration of added  $\text{CoO}$  was 2; 4; 10; 15 mas. %. The specific surface, measured by volume method was about 4.6

$\text{m}^2/\text{g}$ . Greek walnut shells (GWS) and grape seeds (GS) carbonization was held in argon current in a quartz reactor, 0.5- 0.8 mm fraction was used for the experiment. Process temperature  $T = 25-900$  °C, carbonization time is 1 hour.

### *Physicochemical method investigation*

The experiments on carbon sediments process kinetic parameters research was held at thermogravimetric analysis apparatus "Dyupon-951". Every experiment consisted of two stages: sample reduction and sample overcarbonization. Reduction was carried out under non-isothermic conditions in hydrogen stream with heating rate  $20^\circ\text{C}/\text{min}$  to temperature  $450^\circ\text{C}$ . Then the sample was cooled in argon atmosphere to the room temperature, and after that overcarbonization was carried out in methane and argon stream ( $\text{CH}_4$ :  $\text{Ar} = 2:1$ ). The experiment method is described in detail in [10].

For determination of morphology and carbon formations microstructure electron-microscopic analysis with the aid of IBM-LC 100 was held. Samples had been triturated preliminarily and dispersed in alcohol at 70 kHz frequency for 5 or 7 min. X-ray analysis of initial and overcarbonized samples was held with the aid of diffractometer 'DRON-05' at accelerating voltage 35 kV and with using of tubes with cupric cathode (nickel shield). The filming was held with 2 gram/min rate, by diagram band  $-600$  mm/h in angle interval from 2 to 500 degree.

Mossbauer spectra were obtained by dint of device. ESR spectra measurements were held at room temperature with aid of ESR spectrometer of homodine type, working in 3 cm range.

## Results and discussion

### *Kinetics of carbon sediments process*

The rate, activation energy and temperature of carbon formation beginning at methane decomposition on the surface of zeolite -  $\text{CoO}$  mixture have been investigated by method of thermogravimetric analysis (TGA) [11]. Fig.1. shows TGA curves, obtained at overcarbonization of initial zeolite without metal oxide addition. Similar, as in case of investigation of similar systems "metal on a carrier",  $\text{ZrO}_2$ - $\text{Ni}$  [10] pure zeolite doesn't display any catalytic properties up to temperature  $\gg 1000^\circ\text{C}$ .

At higher temperatures the process of carbonaceous sediments formation occurs less intensively, than for the samples with metal addition, and it is due to a

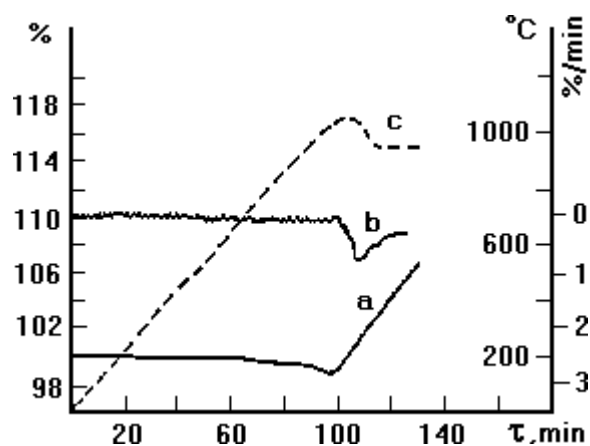


Fig.1. TGA curves of overcarbonization process of pure zeolite: a - change in sample mass (%), b - rate of change in sample mass (%/min), c - curve of temperature increase.

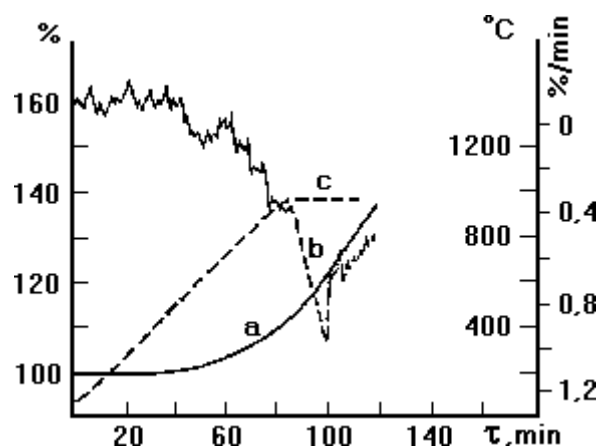


Fig.2. TGA curves of overcarbonization process of zeolite with CoO addition : a - change in sample mass, b - rate of change in sample mass, c - curve of temperature increase.

simple thermal non-catalytic decomposition of metal on the surface of zeolite [11]. For the samples with cobalt oxide addition the process of overcarbonization occurs in a wide temperature interval (Fig.2.). All TG curves, obtained for mechanical zeolite-CoO mixtures, have identical form at different origin temperatures of overcarbonization. It may be seen from Fig.2 that the curves of rate of change in mass contrary to  $ZrO_2$ -Ni [1] and SINP-8-Ni [11] systems have very narrow low temperature region, which is higher than 750 °C.

Studying the dependencies of overcarbonization beginning temperature and cobalt yield on hydrocarbon upon the composition of heterogeneous mixture it is found out The value of change in overcarbonization beginning temperature (curve 1) decreases with an increase of CoO content, and a character of carbonaceous sediments mass gain (curve 2) increases with an increase of metal concentration in mixture. It is seen from these data, that mechanical

adding of CoO practically doesn't influence the coke formation in the low-temperature region and influences significantly on this process in the high-temperature region. Main quantitative characteristics of overcarbonization process of zeolite containing samples are shown in the Table 1.

In connection with the assumption about negligible influence of CoO on the process of coke deposition on the surface of heterogeneous mixture the calculations were made on the results of experiment without division into low-temperature and high-temperature regions. The kinetic parameters - activation energy preexponential factor (Fig.3).- were calculated. Equation  $dm/dt = K_0 e^{-E_0/RT}$  was used for quantitative processing of TGA data.

When CoO is added from 2 to 10% an increase of  $E_0$  and  $K_0$  values is observed. Probably, it may be explained by physical processes, occurred on the surface. Pores of zeolite and the surface of reduced me-

**Table 1**

Main results of experiments on overcarbonization of heterogeneous zeolite - CoO mixture with methane.

CoO, mas. %	Sample mass, mg	Overcarbonization beginning temperature, °C	Mass of carbonaceous sediments for 120 min, mg	Gain in sample mass owing to overcarbonization, %	$E_0$ , kJ/mol	$\lg K_0$
0	27.70	910	2.44	8.8	42.1	3.44
2	29.34	580	10.16	34.6	104	4.74
4	31.81	500	14.31	44.9	136	7.12
10	26.54	480	15.23	57.4	148	8.21
15	27.43	400	17.12	62.4	117	6.83

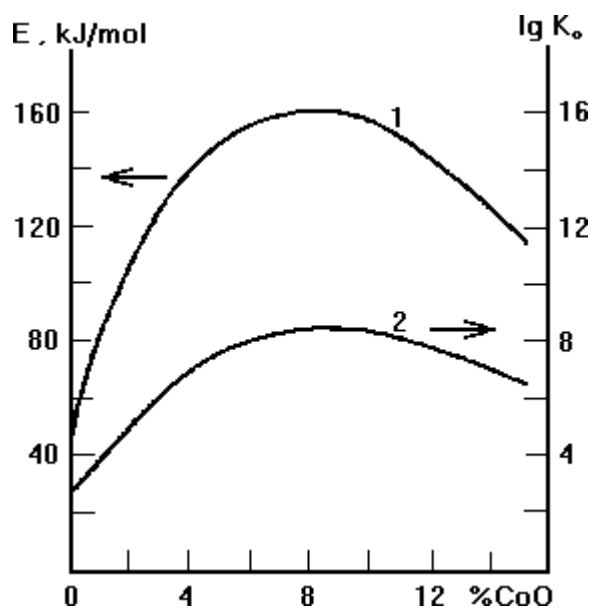


Fig.3. Activation energy  $E_0$  (1) and preexponent  $K_0$  (2) dependence upon the composition of mechanical zeolite - CoO mixture.

tallic particles are completely covered with carbon layer.

The width of this layer influences on the process kinetics and henceforth defines the sorptional properties of sample.

Thus, the dependencies of carbonaceous sediments formation on natural zeolite in mixture with cobalt oxide (II) upon the reaction temperature and ratio zeolite-CoO. With an increase of CoO content in the sample the mass of carbonaceous sediments increases linearly.

#### Structure and physicochemical characteristics

By overcarbonization one can obtain more large surface with number of active centers greater than initial sample had. Electron-microscopic picture of overcarbonized chrome sludge (Fig.4) from which one can see that formation of carbonaceous sediments leads not only to chemical (formation of carbide of metal and evacuation of carbide to carbon fibril) but also to physical processes – carrying of the particles to carbon mass.

Threadlike carbon is a hollow tube on the ends of which there is a particle of metal which is likely an active catalytic center. It should be pointed out here the formation of branching carbon fiber from one center, appearance of so-called ‘octopus’ phenomenon [4,5]. The detailed research of observed branching is the subject of our future study.

An increase of carbon content with the growth of

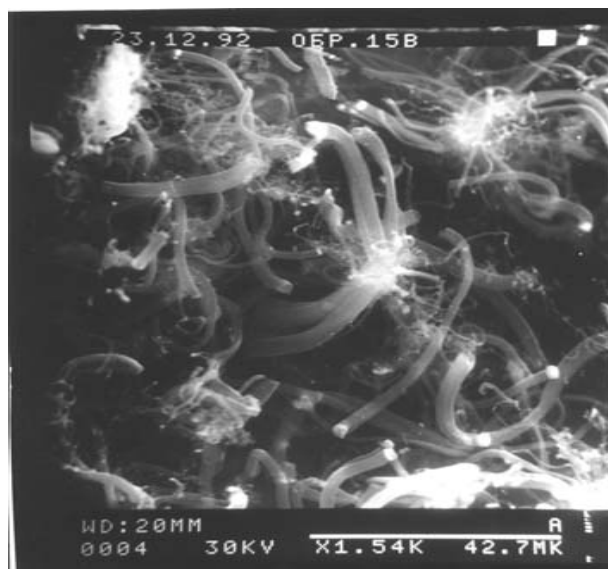


Fig.4. Electron-microscopic picture of overcarbonized chrome sludge at  $T = 800\text{ }^\circ\text{C}$ .

overcarbonization temperature was studied in the temperature interval of 500-800 $^\circ\text{C}$ . Fig 5 represents the graph of dependence of percentage carbon content on temperature, from which one can see that the greatest content of carbon is observed at 800 $^\circ\text{C}$ . Further increase of temperature results in a decrease of carbon amount which is likely connected with decomposition of carbonaceous compound.

The peaks, corresponding to ferric carbide, chromium carbide, silicon carbide and the same elements in free stage, are observed on the rentgenogram of overcarbonized sample of chrome sludge

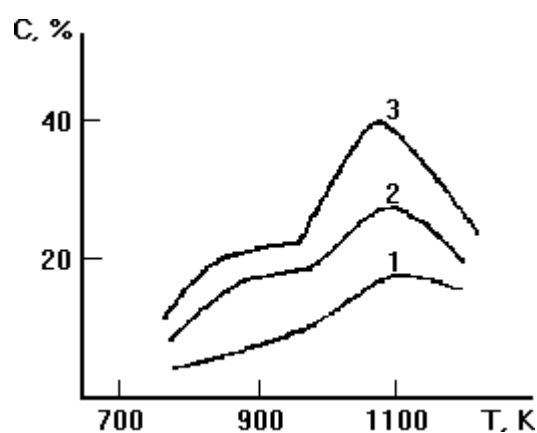


Fig.5. Dependence of percentage carbon content on overcarbonization temperature ( $t = 60\text{ min}$ ): 1- chrome sludge; 2- chrome sludge + 4% CoO; 3- chrome sludge + 4% NiO

(Fig.6).

For FeC intensities of peaks match for angles of rotation 22,5; 32,7 and reflexes of reflection 2,01 and 1,42 on upper layers. Formation of carbides and precipitation of metals in pure form were confirmed by X-ray analysis.

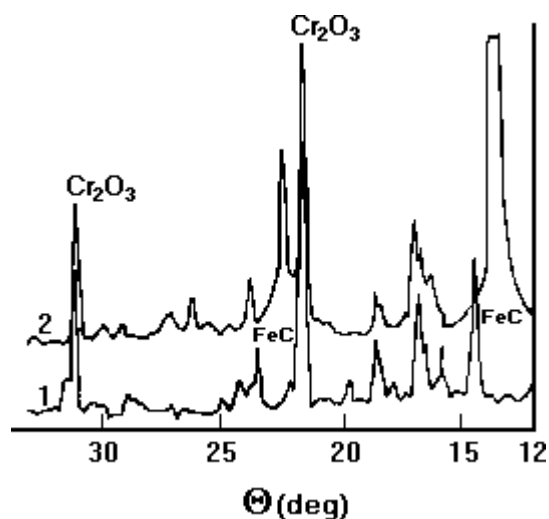


Fig.6. Rentgenogram of chrome sludge + 4% NiO system: 1 – nonovercarbonized sample; 2 – overcarbonized sample at  $T = 800\text{ }^{\circ}\text{C}$ ,  $t = 60\text{ min}$ .

Study of process of carbon pyrolysis showed that overcarbonization depends significantly on temperature, time, gas-flow rate and amount of d-metals in sorbent sample.

#### Mossbauer spectra for overcarbonized samples

Mossbauer spectra for samples of chrome sludge with CoO, overcarbonized at  $T = 750\text{ }^{\circ}\text{C}$  for times of 20, 40, 60, 80 min, are presented in Fig.7; they can be classified into two groups. One of the groups contains original and the first sample, overcarbonized for  $t = 20$  min, are an asymmetrical doublet, the second one contains the second, the third and the fourth samples (40, 60, 80 min respectively), where six-lines spectrum is added to the same doublet.

The asymmetrical spectrum doublet is the superposition of two doublets which present in all spectra and have almost equal parameters. The doublet with lesser isomeric shift corresponds to three-valence iron ions in a tetrahedral surrounding and with greater one - to three-valence iron ions in a octahedral one. Spectrum components area as a first approximation corresponds to relative content of iron in each component.

The component ratio in the original sample is 2:3

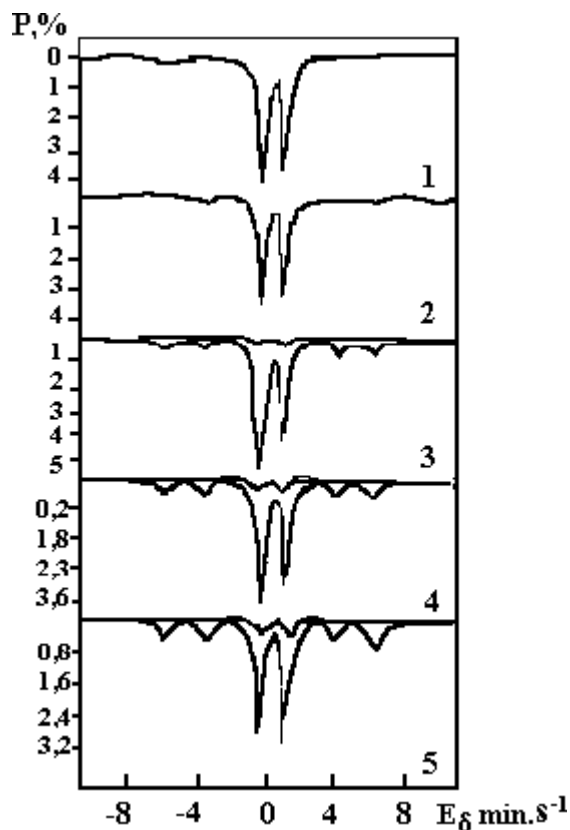


Fig.7. NGR-spectra of chrome sludge + CaO(4%) system, overcarbonized at  $T = 800\text{ }^{\circ}\text{C}$ : 1 – original sample; 2 –  $t = 20$ ; 3 –  $t = 40$ ; 4 –  $t = 60$ ; 5 –  $t = 80$  min.

(40% and 60%). After minimal overcarbonization exposure ( $t = 20$  min) the component ratio changes in favor of the component with tetrahedral surrounding, i. e. iron ions state in octahedral surrounding is less stable in terms of overcarbonization. The third and the fourth spectra verify that: at the overcarbonization time increase the portion of the component with octahedral surrounding decreases.

With the further overcarbonization time increase the portion of the component with tetrahedral surrounding starts to decrease (sample 5).

A sextet appears in spectra from the third sample and it corresponds to metal iron ( $E_{\sigma} = 0$ ).

At the prolonged overcarbonization (samples 4 and 5) the sextet component portion in spectra increases (17% and 24%), though sextet isomeric shift increases (0.02 and 0.04 correspondingly) which is, probably, connected with iron metal phase overcarbonization. The field increase at a nucleus also verifies that.

Parameters obtained after computer treatment of these spectra, are present in Table 2, where  $E_s$  is an isomeric shift relatively to metallic iron,  $E_Q$ , mm/s is

**Table 2**  
Mossbauer spectra characteristics for chrome sludge samples.

Sample	$E_{\sigma}$ , mm·s <sup>-1</sup>	$E_Q$ , mm·s <sup>-1</sup>	H, kO.e.	S, %
1	0,17	1, 46	-	40
	0,36	1,52	-	60
2	0,16	1,51	-	46
	0,34	1,60	-	54
3	0,0	-	335	9
	0,16	1,53	-	46
	0,36	1,62	-	45
4	0,02	-	336	17
	0,20	1,51	-	48
	0,37	1,61	-	35
5	0,04	-	337	24
	0,20	1,45	-	41
	0,30	1,66	-	35

a quadrupolar splitting, H is a field at iron nuclei, kO.e., S is a relative content of a component percentage.

#### *ESR of overcarbonized samples*

Studied chrome sludge is a rather complex multi-component system, some components of which can influence significantly on process of its overcarbonization.

In this connection the study of overcarbonization process in more simple systems such as, for example, Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> oxides with the use of ESR is of interest. Analysis of samples overcarbonized at 400, 500, 600, 700 °C temperatures was held.

Fe<sub>3</sub>O<sub>4</sub> oxide is magnetic-concentrated material and it shows ferromagnetic properties even at room temperature. Dependence of magnetic resonance signal strength upon Fe<sub>3</sub>O<sub>4</sub> carbonization temperature is illustrated in Fig.8.

Big width of lines, changing from 1820 R.u to 2835 R.u. is the characteristic feature of spectra of both original Fe<sub>3</sub>O<sub>4</sub> sample and overcarbonized at different temperatures ones. Intensity of lines increases sharply with sample overcarbonisation at 400 °C and at T<sub>0</sub> = 500 °C it reaches maximum value. Increasing of overcarbonization temperature to 600 °C causes decreasing of signal strength in 20 times. Unfortunately, on this system one also did not manage to register

ESR signal of carbonaceous sediments because of intensive signal from iron.

In this respect, the study of chromiferous system overcarbonization is perspective. Dependence of ESR line intensity upon Cr<sub>2</sub>O<sub>3</sub> sample overcarbonization temperature is presented in Fig.9.

One can see that maximum strength of ESR signal is reached with the first overcarbonisation tempera-

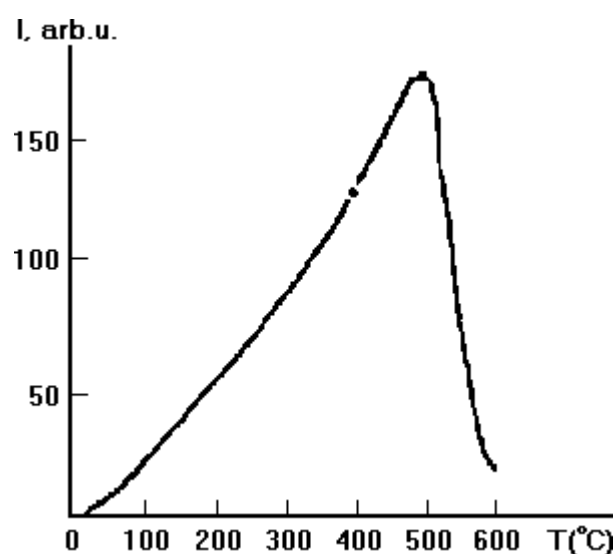


Fig.8. Magnetic resonance intensity dependence on overcarbonization temperature for Fe<sub>3</sub>O<sub>4</sub>.

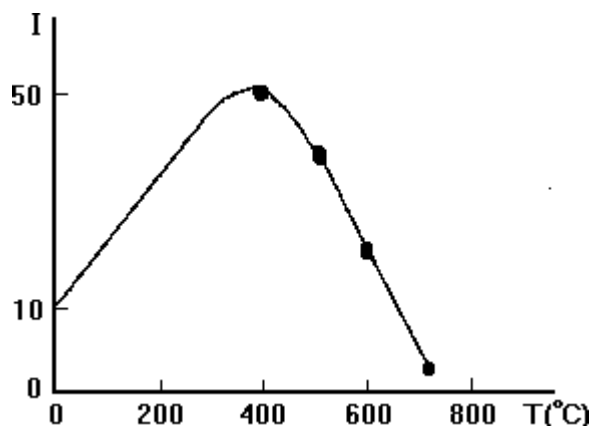


Fig.9. Magnetic resonance intensity dependence on overcarbonization temperature for  $\text{Cr}_2\text{O}_3$ .

ture  $T_{\max} = 400\text{ }^\circ\text{C}$  and exceeds strength of original sample signal in only 4,6 times. It is on almost 2 orders less than for  $\text{Fe}_3\text{O}_4$ .

Strengths of magnetic resonance signals in studied  $\text{Fe}_3\text{O}_4$  and  $\text{Cr}_2\text{O}_3$  systems have some mutual inherent tendencies depending on overcarbonisation temperature. They all pass through maximums, but at different temperatures, and then their values decrease sharply. Fig. 10 presents ESR spectra, obtained from original chrome oxide (a), at overcarbonization temperature  $500\text{ }^\circ\text{C}$  (d) and at overcarbonisation temperature  $700\text{ }^\circ\text{C}$  (c).

All spectra were registered at room temperature. One can see that original ESR spectrum is wide line of weak intensity 1870 R.u. wide, and a line of weak intensity but less wide puts over this spectrum. This, probably, indicates the fact, that there are strange admixtures, at least of two types, in the studied chrome oxide. For clearing up the nature of wide line the registration of small amount of iron oxide spectrum is laid over the registration of this spectrum (Fig 10-b). Good enough coincidence of these lines allows to conclude that principal admixture in chrome oxide is iron oxide.

Chrome oxide is yet the only system of studied ones in which one managed to register ESR signal from carbonaceous sediments. It is worth noting that there is a weak signal with  $g = 4,3$  of  $\text{Fe}^{3+}$  ions in the same sample. This, probably, indicates the fact, that small part of isolated  $\text{Fe}^{3+}$  ions at this temperature is included in complexes with strong lowsymmetrical crystalline field. The appearance of signal also confirms the presence of admixture iron in studied sample.

It is worth noting that strength of signal at over-

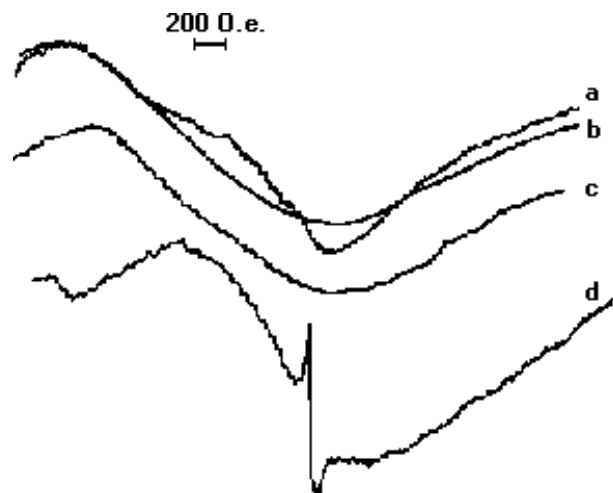


Fig.10. Magnetic resonance signals for  $\text{Cr}_2\text{O}_3$  at different overcarbonization temperatures: a– origin chrome oxide; b– a signal for  $\text{Fe}_3\text{O}_4$ ; c -  $\text{Cr}_2\text{O}_3$  – overcarbonized at  $T = 700\text{ }^\circ\text{C}$ ; d —  $\text{Cr}_2\text{O}_3$  – overcarbonized at  $T = 500\text{ }^\circ\text{C}$ .

carbonization temperature  $700\text{ }^\circ\text{C}$  is in 2,7 times less than original one. In studied systems one did not observe such sharp decrease of signal strength at terminal overcarbonization temperatures.

This allows on the sample overcarbonized at  $700\text{ }^\circ\text{C}$  to register signal of carbonaceous sediments with line  $\Delta H = 34\text{ O.e.}$  and  $g = 2,002$  against the background of the weak signal of admixtures. Value of  $g$ -factor is very close to its pure spin value that allows to suppose that the signal is caused by free carriers in graphitic formations.

### Sorption properties studying

Sorption capacity of obtained sorbents was studied for absorption of phenol from aqueous solution. One can see from Table 3 that overcarbonized mixture of clay with chrome sludge (1: 30) holds sorption of phenol with 98,7%.

$\text{SO}_2$  adsorption on overcarbonized at thermocatalytic pyrolysis of propane-butane mixture in temperature range of  $400\text{--}800\text{ }^\circ\text{C}$  Naryncol clay and on clay which was soaked with Ni preliminarily was studied by method.

Naryncol clay purely sorbs  $\text{SO}_2$ , which is only  $0,36\text{ cm}^3/\text{g}$ . Carbon modified Naryncol clay increases quantity of sorbed and desorbed  $\text{SO}_2$  to  $8,76\text{ cm}^3/\text{g}$ . The biggest quantity of adsorbed  $\text{SO}_2$  ( $13,52\text{ cm}^3/\text{g}$ ) is obtained on clay with 5% Ni content, overcarbonized at  $T = 500\text{ }^\circ\text{C}$ . At the catalyst thermodesorption a small carbon portion was removed from it and sulfur dioxide was extracted with desorption activation energy

**Table 3**

Phenol sorption by overcarbonized mixture of clay with chrome sludge (1:30).

No	Adsorbent	Phase ratio, g/l	Purification degree, %
1	Nonovercarbonized chrome sludge	1:10	68,0
2	Clay	1:10	72,7
3	Overcarbonized clay	1:10	95,9
4	Overcarbonized clay with chrome sludge (1:1)	1:10	97,7
		1:20	97,0
		1:30	98,7
		1:40	97,0
		1:50	98,5

values less than in comparison with SO<sub>2</sub> desorbing on overcarbonized clay without Ni addition.

It was found out at overcarbonization temperature increasing the desorbed SO<sub>2</sub> quantity also increased. By method of electron microscopy it was shown that in sorption process threadlike carbon decomposition at the catalyst surface occurred, thus carbon fiber diameter decreased.

It was verified that carbon modified Ni catalyst is effective in gaseous exhaust purification process. Comparing with known in literature Pt-Pd/g- Al<sub>2</sub>O<sub>3</sub> catalyst, the quantity of absorbed SO<sub>2</sub> increased in 3.5 times.

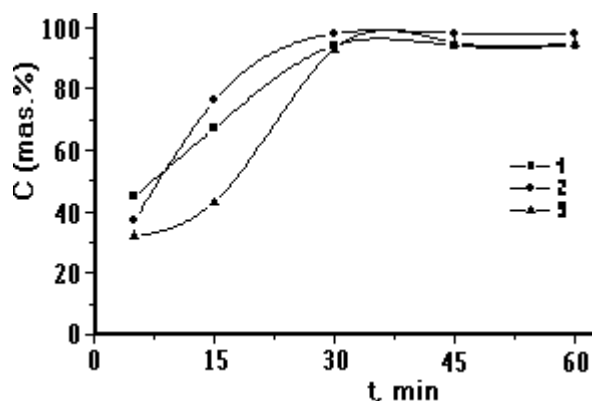


Fig. 11. Kinetics of metal absorption by GWS sorbent. The curves: 1 – Cu<sup>2+</sup>, 2 – Cd<sup>2+</sup>, 3 – Pb<sup>2+</sup>.

#### Carbonized sorbents on the base of Greek walnut shells (GWS) and grape seeds (GS)

The raw material on the base of agricultural wastes reprocessing refers to restored sources is safe for the environment. At walnut shell and grape kernel samples carbonization the main mass loss takes place at the temperature range 200 – 500 °C (Fig. 11). At T = 500 °C 50% of mass is lost in an hour and, finally, 75% is lost at T = 950 °C.

By method of Ar thermal desorption the sample specific surfaces were defined. Specific surface, porosity and density of sorbents, treated at different temperatures, are given in Table 4.

**Table 4**

Effective surface, porosity and density of overcarbonized samples.

Overcarbonization temperature, °C	Sorbents	Density g/cm <sup>3</sup>	Porosity, cm <sup>3</sup> ·g <sup>-1</sup>	Specific surface m <sup>2</sup> /g
25	OWS	1,64	0,23	100
	OGP	1,52	0,16	95
300	OWS	1,23	0,75	250
	OGP	0,94	0,38	200
400	OWS	0,82	0,94	560
	OGP	0,63	0,76	400
500	OWS	0,76	1,48	770
	OGP	0,62	1,0	490
600	OWS	0,41	1,49	780
	OGP	0,36	1,13	500
800	OWS	0,30	2,3	830
	OGP	0,33	2,2	540



As one can see from the table the specific surface of active carbons on the base of WS increases from 250 to 780 m<sup>2</sup>/g, the one on the base of GP increases from 200 to 500 m<sup>2</sup>/g.

The largest specific surface of active carbons was observed at T = 800 °C, however the product outlet at this temperature decreased in almost two times in comparison with T = 700 °C. The specific value decrease was at the temperature higher than T = 800 °C.

The carbonized samples sorption capacity was tested at hard metal ions absorption.

After transmission of studying solutions through active carbons by method of atomic – absorptional analysis it was found out that synthesized active carbons sorb Cu<sup>2+</sup> and Pb<sup>2+</sup> ions effectively. The solutions were prepared at metal ion concentration which exceeded maximum allowable concentration in 10 times.

The data on the kinetics of metal absorption by OWS sample are given at Fig.11.

As one can see from Fig.11 the sorption value reaches almost 100% for a small time interval. The high sorption capacity can be explained due to active carbons structure and chemical sorption caused by interaction of functional groups at the surface.

#### *Metal-carbon catalysts of hydrocarbon cracking*

Cracking of propane-butane mixture on cobalt (nickel, palladium)- carbon catalysts has been studied. Carbon - cobalt catalysts are the best.

Fig.12 shows temperature dependencies of olefins and aromatic compounds yield.

The results obtained show that products of reaction are olefins (ethylene, propylene, iso-propylene), aromatic compounds (benzene, toluene, ethylbenzene, xylene) and also hydrogen, methane, ethane, propane,

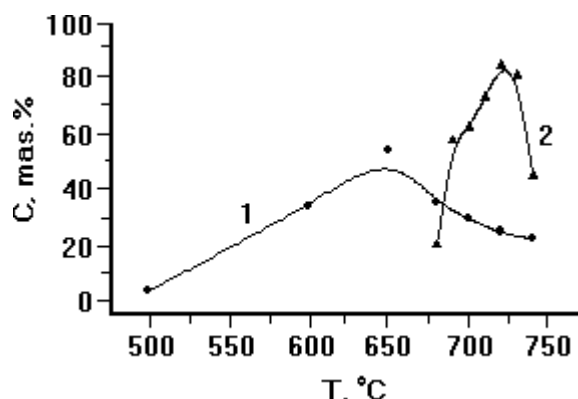


Fig.12. Temperature dependence of olefin and aromatic compound yield. 1 –olefin yield; 2 – aromatic compound (benzene, toluene, xylene, ethylbenzene) yield.

butane and iso-butane.

Fig.12 shows that in temperature interval 500-740 °C it is observed that maximum quantity of olefins is formed at 650 °C, 53,5 mas.%. In the presence of overcarbonized cobalt catalyst aromatic compounds yield is 84,7 mas.% at 700 °C. With increasing of temperature aromatic compounds yield decreases to 44,9 mas.%. The obtained data show that aromatic compounds formation has narrow temperature range.

#### *Improved refractory materials obtaining*

Earlier effective nonshaped SHS refractory materials on the base of chrome concentrated were worked out in works of M.B. Ismailov and his colleagues [12]. With the aim of utilization and using of reasonable and cheap raw materials partial substitution of chrome concentrate by chrome sludge was made [4]. Data of obtained refractory materials are presented in Tables 5,6.

From the given Tables (5,6) it is seen that chrome

**Table 5**

Physicomechanical characteristics of refractory materials with overcarbonized chrome sludge addition.

Refractory materials	Temperature of inflammation, °C	Temperature of combustion, °C	σ, compression, MPa	Porosity, %	Density g/cm <sup>3</sup>
Additions C + Chrome sludge, %					
1	830	1300	9,6	30,1	2,31
2	840	1400	22,8	16,8	2,82
3	930	1490	28,4	13,5	3,13
4	920	1450	16,4	23,0	3,21
5	900	1380	13,2	27,0	3,34
"Phurnon-3XP"	827	1497	11	-	-

**Table 6**

Physicomechanical parameters of carbon refractory materials on the base of Chilyc clay.

Addition C + Chrome sludge, %	Temperature of inflammation, °C	Temperature of combustion, °C	$\sigma$ compression, Mpa	Porosity, %	Density g/cm <sup>3</sup>
0	830	1400	6	26,22	4,5
3	820	1350	6,4	25,55	5,8
5	800	1250	7,2	24,87	6,4
7	900	1380	8,0	24,27	4,2
10	900	1400	9,6	24,57	3,7

sludge adding increases density and mechanical solidity in comparison with refractory “Phurnon – 3XP” improving refractoriness insignificantly.

The improvement of carbonaceous refractory materials physicomechanical indexes on clay and chrome sludge base is explained due to carbon and metal carbide formation.

### Conclusion

From the given results it can be concluded that the adsorptive-catalytic systems on chrome and bauxite sludge and clay base are used successfully as sorbents for wastewater purification and refractory materials with improved properties due to increased specific surface and active metal centers.

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