

Carbon Containing Compositions

R.M. Mansurova, Z.A. Mansurov

Combustion Problems Institute
480012, Almaty, 172, Bogenbai Batyr Str., Kazakhstan

E-mail: mansurov@lorton.com

The experiment established optimal conditions for over-carbonization. With the use of the electron microscopy and X-ray phase analysis the regularities of carbon deposit formation in process of methane and propane pyrolysis on the zeolites, Kazakhstan natural clays, chrome and bauxite sludge containing metal oxides of iron subgroup, have been studied. In process of over-carbonization the trivalent iron was reduced to metal form. In addition, the carbon tubes of divers morphology had been impregnated with ultra-dispersed metal particles. The kinetic parameters of carbon formation in process of methane decomposition on the zeolite – CoO mixture surface were investigated by method of thermo-gravimetric analysis. The morphology and structure of formed carbon fibrils, with the metal particles fixed at their ends, have been investigated, the formation of branched carbon fibrils pattern, so called octopus, being found. Also, the walnut shells and grape kernel carbonization, their immobilization by the cells of selective absorption of heavy metal and sulfur dioxide ions have been studied. The examples of metal-carbon composites used as adsorbents for wastewater purification, C₃- C₄ hydrocarbon cracking catalysts and refractory materials with improved properties have been considered.

Keywords : carbon, carbonization, environment protection

1. INTRODUCTION

Carbon containing materials are considered to be promising for solving the problems of environment protection from pollution, purification of sewage disposal, separating valuable components from them. The high thermal, chemical and radiation resistance of fibrous coals makes possible to use them in more severe regimes of exploitation compared to polymer sorbents. Contrary to grain absorbents the fibrous coals are characterized by their greater rate and complete sorption-desorption processes [1,2].

A number of papers have been devoted to inherent tendencies and mechanism of carbon fibril formation. Carbon deposit formation was proceeded by carbide mechanism, offered by Buyanov R.A [2].

According to this mechanism, the reduction of material, itself interacting with hydrocarbons with formation of carbides, takes place when such hydrocarbons interact with oxides. Decomposition of carbides gives rise to the formation of iron and free

carbon that may serve as a base of carbon deposits formation of divers structures.

Carbon monoxide, hydrocarbon gases and liquids are the raw materials for catalytic carbon obtaining, while metal oxides, sludge and clays are used as catalysts-carries. Over-carbonization was achieved through the use of flow reactor in carbon pyrolysis process on the surface of salts or metal oxides of transition elements (pyrolysis is carried out at temperature range from 350 to 1025 °C).

As a result of the pyrolysis the catalytic carbon with up-rated specific surface exceeding ordinary sizes by five or ten times, is formed on the catalyst surface. It is due to the morphology of carbon deposits, being fibril, tube formation and clusters of 1500 –3000 Å diameters. Besides, there is occurred dissemination of metal particles of 200-800 Å diameter.

It is necessary to underline that the carbon fibril formation has sophisticate character and sometimes gives rise to branched structures evidenced by the fact that one metal particle initiates formation of several

carbon fibrils in different directions, so-called 'octopus' effect [2-5].

Recently the experts involved in carbon material technology (CM) pay especial attention to the process of catalytic cracking of hydrocarbons. It has been determined that Fe, Ni, Co, their oxides as well as alloys of these metals are the most efficient catalysts. As a result of catalytic reaction the formation of carbonaceous deposits is noted for dispersed metal particles. These deposits have specific shapes and properties enabling to consider them as very promising ultra-dispersion systems, used in divers fields of chemistry. Last years some experimental materials have been obtained providing metal-carbon composite applications as adsorbents, catalyst-carriers and catalysts of the number of chemical reactions.

Recently the works aimed at obtaining of over-carbonized materials on the base of local clays and mining industry waste that are chrome and bauxite sludge, agricultural wastes (walnut shells and grape kernels) and their application are carried out in the Kazakh NSU's 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 SO₂ and for production of improved refractory materials used as catalyst carriers and hydrocarbon conversion reaction catalysts. The results of such systems investigation and data on their synthesis obtained by the authors and colleagues are given below.

2. EXPERIMENTAL

2.1. Substances and over-carbonized samples preparation

Over-carbonization of chrome sludge was carried out in flow running conditions in the quartz reactor (d=30mm) with propane-butane mixture (60%+40%).

A pounded fraction (a=0,25-0,5mm) fed by (30g) charges into the reactor was used in this experiment.

The process was carried out at temperatures T = 500-800 °C, time of contact being t = 20-80 min, gas flow rates up to 3-7 l/hour. Carbon content of over-carbonized samples was estimated by combustion of the sample of 1-2 g mass placed in ceramic boat in the horizontal tube furnace at the temperature T = 800 °C for 40 minutes. Carbon concentrations were determined as sample mass differences before and after combustion.

Natural zeolite of Altyn-Amel deposit in Kazakhstan has an averaged composition (%): SiO₂ 47.9; TiO₂ 0.84; Al₂O₃ 17.6; Fe₂O₃ 0.6; FeO 0.6; MnO 0.12; CaO 7.3; MgO 4.7; Na₂O 2.6; K₂O 0.5; P₂O₅ 0.1; SO₃ 0.1.

Zeolite was granulated in laboratory conditions China clay being added as binder. Cobalt oxide (11) was added by mechanical mixing with beforehand ground zeolite (0.5 mm). Concentrations of added CoO were 2; 4; 10; 15 mass %. The specific surface measured by volumetric method was about 4.6 m²/g. Walnut shells (WS) and grape kernels (GP) carbonization was proceeded in argon flow in quartz reactor, the 0.5- 0.8 mm fraction being used in this experiment. The process temperature T = 25 – 900 °C, carbonization time 1 hour.

2.2. Physicochemical investigation method

The experiment aimed at investigation of kinetic parameters of carbon deposit formation process was carried out by thermo-gravimetric analysis in the «Dyupon-591» unit. Every experiment consisted of two stages: sample reduction and sample over-carbonization. The reduction was carried out in non-isothermal conditions in hydrogen stream at heating rate 20°C/min to temperature 450°C. Then the sample was cooled in argon atmosphere to the room temperature, and after that over-carbonization was carried out in methane and argon stream (CH₄: Ar = 2:1). The experiment method is described in detail in [1].

The morphology and carbon microstructure formations were determined by electron-microscopic analysis using the IBM-LC 100 unit. The sample was placed on the holder that then was placed in a vacuum plant. Then by ionic dispersion method the thin structureless gold layer was spread on the support to improve object photograph quality. Then the holders with studied samples were placed in the electron probe analyzer and photographed in regime of secondary electrons at divers amplifying rates to improve photograph quality. X-ray phase analysis of source and over-carbonized samples was carried in the 'DRON-05' diffractometer at accelerating voltage 35kV and with using of tubes with cupric cathode (nickel shield). The filming was proceeded at 2 g/min rate within 600mm/h diagram band, the angle interval being from 2 to 500 degree.

Mossbauer spectra were obtained by ESR spectrometry method at room temperature using the ESR spectrometer of homodine type, working in 3-cm range.

3. RESULTS AND DISCUSSION

3.1. Kinetics of carbon deposits process

In this work the rate, activation energy and temperature of carbon formation occurred in process of methane decomposition on the surface of zeolite - CoO mixture have been investigated by thermogravimetric analysis method (TGA). In the Fig.1 the TGA curves obtained in process of initial zeolite over-carbonization

without metal oxide addition are presented. Similarly as in case of analogous systems investigation the «metal on a carrier», ZrO_2 -Ni [1], SINP-8-Ni [6], pure zeolite shows no catalytic properties up to temperature $\approx 1000^\circ C$.

At higher temperatures the process of carbonaceous deposits formation occurs less intensively, than for the samples with metal addition, and it is due to the simple thermal non-catalytic decomposition of metal on the surface of zeolite [11]. For the samples with cobalt oxide addition the process of over-carbonization occurs in a wide temperature range (fig.2.). All TG curves, obtained for mechanical zeolite-CoO mixtures, have identical form at different initial temperatures of over-carbonization. As may be seen from the fig.2 the curves of mass change rate, contrary to ZrO_2 -Ni [1] and SINP-8-Ni [11] systems, have very narrow low temperature region exceeding $750^\circ C$.

The low temperature process of carbon deposits formation is running through intermediate compounds resulted of propane adsorption on the acid centers created at certain temperatures on the catalyst. Likely, such intermediate compounds should migrate to the centers where the further coke formation is occurred. There isn't excluded the participation of active metal centers at second high temperature stage of coke formation since in process of over-carbonization of pure samples, i.e., in absence of active metal centers, the coke formation is noted at $1000^\circ C$ temperature. While on the zeolite with nickel additions the second stage of over-coking is starting at $650^\circ C$.

Basing on the investigation results there were obtained dependencies of the temperature of over-carbonization starting and carbon yield on the heterogeneous hydrocarbons mixture compositions. The value of change in over-carbonization starting temperature (curve 1) decreases with an increase of CoO content, and the value of gain in carbonaceous deposits mass (curve 2) increases with an increase of metal concentration in mixture. As is evident from these data, the mechanical adding of CoO practically effects no the coke formation in the low-temperature region while its significant effects being noted for high-temperature region of this process. The major quantitative characteristics of over-carbonization process of zeolite containing samples are shown in the table 1.

Assuming effects of the CoO on the process of coke deposition on the surface of heterogeneous mixture as negligible ones, the calculations were based on the experiment results taking no in consideration the differences for low-temperature and high-temperature regions. The kinetic parameters, i.e., activation energy pre-exponential factor (fig.4), were calculated. The

equation $dm/dt=K_0e^{-E/RT}$ was used for quantitative processing of TGA data.

When the CoO is added in amounts from 2 to 10%, the increase of E_0 and K_0 values is observed. Probably, it may be explained by physical processes occurred on the surface. The pores of zeolite and the surface of reduced metal particles are completely covered with carbon layer.

The width of this layer effects on the process kinetics and henceforth defines the sorption properties of the sample.

Thus, the dependencies of carbonaceous deposits formation on the natural zeolite mixed with cobalt oxide (II) on the reaction temperature and zeolite-CoO ratio are obvious. The CoO content of the sample being increased the mass of carbonaceous deposit gains linearly to it.

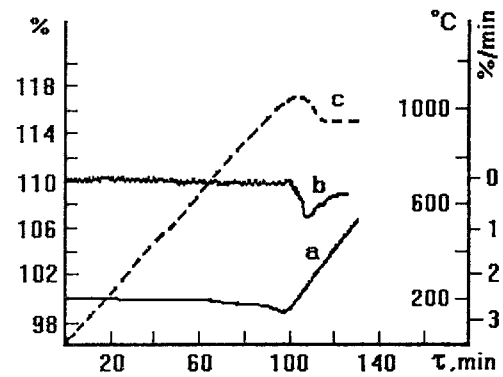


Fig.1. TGA curves of over-carbonization process of pure zeolite: a - change in sample mass (%), b - rate of change in sample mass (%/min), c - curve of temperature increase.

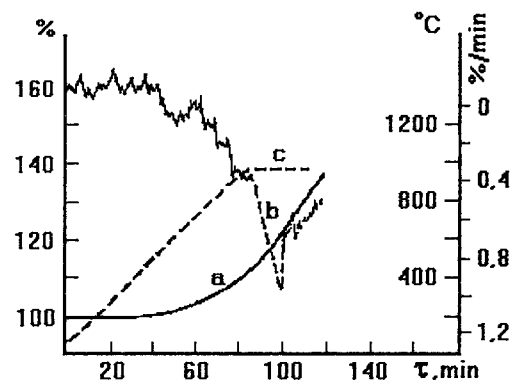


Fig.2. TGA curves of over-carbonization process of zeolite with CoO addition : a - change in sample mass, b - rate of change in sample mass, c - curve of temperature increase.

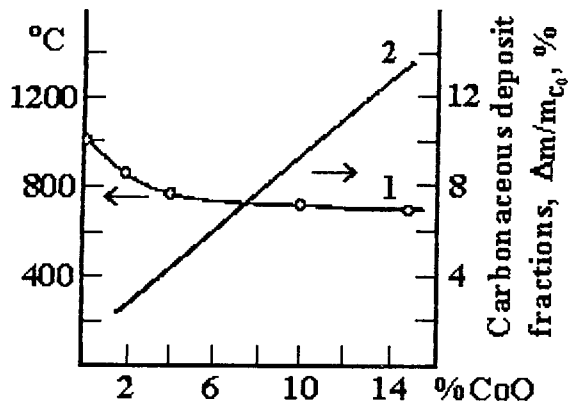


Fig.3. Over-carbonization starting temperature (1) and cobalt yield on carbon dependence upon heterogeneous zeolite - CoO (2) mixture decomposition

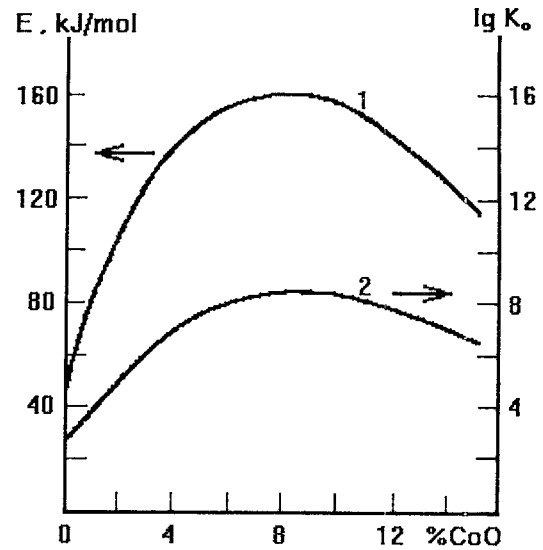


Fig.4. Activation energy E_0 (1) and pre-exponential K_0 (2) dependence on the composition of mechanical zeolite - CoO mixture.

Table 1. Major experiment results of over-carbonization of heterogeneous zeolite - CoO mixture with methane.

CoO, mas. %	Sample mass, mg	Over-carbonization starting temperature, °C	Mass of carbonaceous deposits for 120 min, mg	Gain in sample mass resulting of over-carbonization, %	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

3.2. Structure and physicochemical characteristics

The over-carbonization enables to obtain larger surfaces with a number of active centers exceeding that of source sample. The electron-microscopic photograph of over-carbonized chrome sludge (fig.6) shows that the formation of carbonaceous deposits leads not only to chemical processes (formation of metal carbide and carbide transfer to the carbon fibril) but also to physical processes (carrying of the particles to the carbon mass).

The threadlike carbon is a hollow tube on those ends the metal particle is likely an active catalytic center. The formation of branched carbon fiber starting from one center, the occurrence of so-called 'octopus' phenomenon are noted here [4,5]. The observed branching will be subject of our further thorough investigation. The results obtained by electron microscopy method applied in the RAS Sibir Division's Institute of Catalysis proved that the threadlike carbon

formed in process of chromite sludge over-carbonization is hollow nano-tubes with metal particle on their ends. The carbon has a graphite-like structure evidenced by micro-diffraction method.

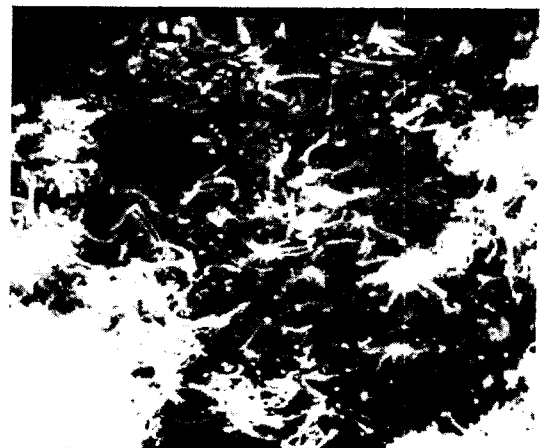




Fig.5. Electron-microscopic photograph of over-carbonized chrome sludge at $T = 800\text{ }^{\circ}\text{C}$.

For FeC the peak intensities are falling at the angles of rotation 22,5; 32,7 and reflexes of reflection 2,01 and 1,42 on upper layers. The formation of carbides and deposits pure metal were confirmed by X-ray phase analysis.

The study of carbon pyrolysis process showed that the over-carbonization depends significantly on the process temperature, time, gas-flow rate and amount of d-metals in sorbent sample.

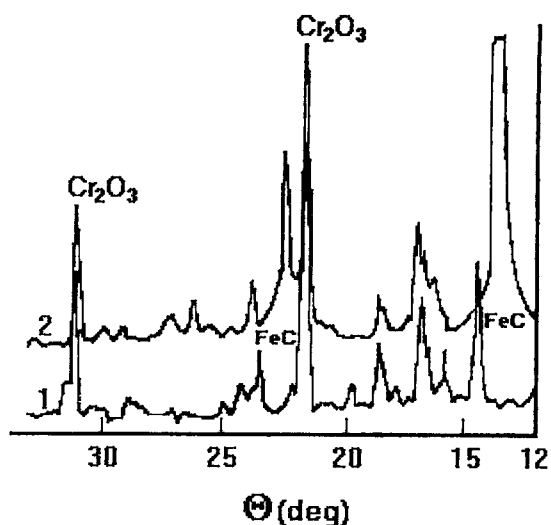


Fig.6. X-ray photograph of chrome sludge + 4% NiO system: 1 – non-over-carbonized sample; 2 – over-carbonized sample at $T = 800\text{ }^{\circ}\text{C}$, $t = 60\text{m}$.

3.3. Moessbauer spectra for over-carbonized samples.

The Moessbauer spectra for the samples of CoO containing chrome sludge over-carbonized at $T=750\text{ }^{\circ}\text{C}$ during exposure time 20,40,60,80 min, are presented in the fig. 7. They can be classified into two groups, one of which containing source sample and first sample over-carbonized during $t=20$ min that are an asymmetrical doublet. The second one contains the second, the third and the fourth samples (40,60,80 min respectively), where the six lines spectrum is added to the same doublet.

Table 2. Moessbauer spectra characteristics for chrome sludge samples

Sample	$E_{\sigma}, \text{mm}\cdot\text{s}^{-1}$	$E_{\text{O}}, \text{mm}\cdot\text{s}^{-1}$	H, kOe	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

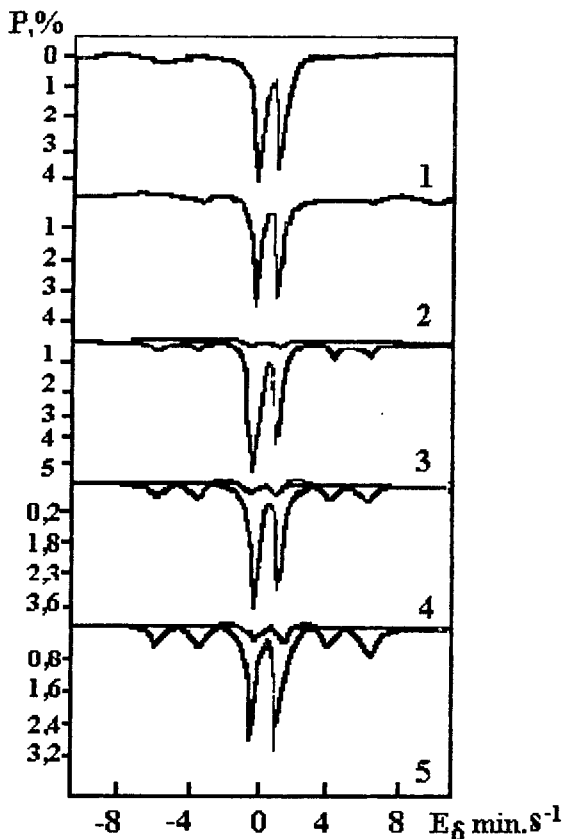


Fig. 7. NGR-spectra of chrome sludge + CaO(4%) system, over-carbonized at $T = 800\text{ }^{\circ}\text{C}$: 1 –source sample; 2 – $t = 20$; 3 – $t = 40$; 4 – $t = 60$; 5 – $t = 80\text{m}$.

The asymmetrical spectrum doublet is the superposition of two doublets available in all spectra and showing almost equal parameters. The doublet with lesser isomeric shift corresponds to trivalent iron ions in a tetrahedral medium and with greater one - to trivalent iron ions in an octahedral medium. The area of spectrum components, as a first approximation, corresponds to relative iron content of each component.

The component ratio in the source sample is 2:3 (40% and 60%). After minimal over-carbonization exposure ($t = 20\text{ min}$) the component ratio changes in favor of the component with tetrahedral medium, i. e. iron ions state in octahedral medium is less stable in terms of over-carbonization. The third and the fourth spectra evidence that with increase of over-carbonization time the fraction of component in octahedral medium decreases.

With further increase of over-carbonization time the portion of component in tetrahedral medium starts to decrease (sample 5).

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

In process of prolonged over-carbonization (samples 4 and 5) the septet component fraction in spectra

increases (17% and 24%), though septet isomeric shift increases (0.02 and 0.04 respectively), that is, probably, due to phase over-carbonization of metal iron. This is proved by field increase at a nucleus.

The parameters obtained by computer processing of these spectra are given in the table 2. There: E_{σ} is an isomeric shift relatively to the metal iron, E_Q , mm/s, is a quadrupolar splitting, H is a field at iron nuclei, kilooersted, S is a relative component content in terms of percentage.

3.4. ESR of over-carbonized samples

The studied chrome sludge is a rather complex multicomponent system those some components may significantly effects on the over-carbonization process.

In this connection the study of over-carbonization process in more simple systems such as, for example, Cr_2O_3 and Fe_3O_4 oxides using ESR method, is of interest. The analysis of samples over-carbonized at 400, 500, 600, 700 $^{\circ}\text{C}$ temperatures were carried out.

The large width of the lines varying from 1820 R.u. to 2835 R.u. is the characteristic feature of the spectra for both original Fe_3O_4 sample and sample over-carbonized at different temperatures. The intensity of the lines sharply increases with sample over-carbonization at 400 $^{\circ}\text{C}$, reaching its maximum value at $T_0=500\text{ }^{\circ}\text{C}$. The increase of over-carbonization temperature to 600 $^{\circ}\text{C}$ results in decreasing of signal strength by 20 times. Unfortunately, in this system it is impossible to manage signal of carbonaceous deposits to ESR register because of intensive signal from iron.

In this respect the study of over-carbonization of chromiferous system is promising. The dependence of ESR line intensity on the Cr_2O_3 sample over-carbonization temperature is presented in the fig. 8.

It is obvious that the maximum strength of ESR signal is reached with first over-carbonisation temperature $T_{\text{max}}=400\text{ }^{\circ}\text{C}$ and exceeds only strength of

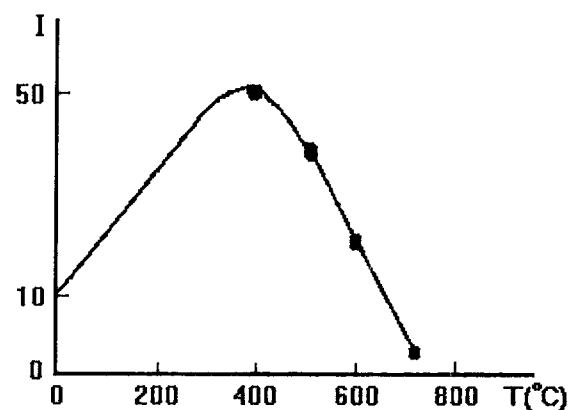


Fig. 8. Magnetic resonance intensity dependence on overcarbonization temperature for Cr_2O_3 .

source sample signal by 4,6 times. It is almost by 2 orders less than for Fe_3O_4 .

The strengths of magnetic resonance signals in studied Fe_3O_4 and Cr_2O_3 systems have some mutual inherent tendencies depending on the over-carbonization temperature. They all pass through maximums, but at different temperatures, and then their values decrease sharply. The fig. 9. presents ESR spectra, obtained for source chrome oxide (1), at over-carbonization temperature 500 °C (3) and at over-carbonization temperature 700 °C (4).

All spectra were registered at room temperature. It is evident that the original ESR spectrum is a wide line of weak intensity 1870 R.u., and a line of weak intensity but less wide puts over this spectrum. This, probably, indicates that there are foreign admixtures, at least of two types, into the studied chrome oxide. To refine the nature of wide line the registered signal for small amount of iron oxide spectrum is overlaid the registered signal of this spectrum (fig 9-b). The good enough coincidence of these lines allows concluding that principal admixture in the chrome oxide is iron oxide.

The chrome oxide is yet the only system of the studied ones making possible to manage ESR register signal from carbonaceous deposits. It is worth noting that there is a weak signal with $g=4,3$ of the Fe^{3+} ions in the same sample. Likely this evidence that the small fraction of separate Fe^{3+} ions at this temperature is included in the complexes with strong low-symmetrical crystalline field. The signal appearance also confirms the presence of iron admixture in the studied sample.

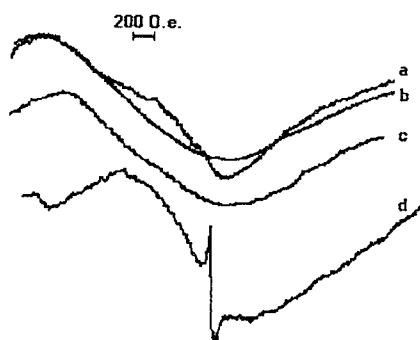


Fig. 9. Magnetic resonance signals for Cr_2O_3 at different over-carbonization temperatures: 1–source chrome oxide; 2– a signal for Fe_3O_4 ; 3 - Cr_2O_3 – over-carbonized at $T = 973 \text{ K}$; 4 -- Cr_2O_3 – over-carbonized at $T = 490 \text{ °C}$.

It is worth noting that the signal strength at 700 °C over-carbonization temperature is by 2,7 times less than original one. In studied systems there weren't observed such sharp decreasing in signal strength at terminal over-

carbonization temperatures. This allows to register signal of carbonaceous deposits with line $\Delta H=34 \text{ Oe}$ and $g=2,002$ for the sample over-carbonized at 700 °C, on the background of the weak signal of the admixtures. The value of g -factor is very close to its pure spin value that allows supposing that the free carriers in graphitic formations cause the signal.

3.5. Sorption properties

The sorption capacity of the obtained sorbents was studied for absorption of phenol from the water solution. As is evident from the table 3 the over-carbonization of the mixture of clay and chrome sludge (1: 30) is proceeding with sorption of 98,7% phenol.

The SO_2 adsorption on the Naryncol clay and on the clay pre-soaked with Ni, in process of propane-butane mixture over-carbonization by thermo-catalytic pyrolysis within temperature range of 400-800 °C was studied by method.

The Naryncol clay purely sorbs SO_2 , which is only $0.36 \text{ cm}^3/\text{g}$. Carbon modified Naryncol clay increases quantity of sorbed and desorbed SO_2 to $8.76 \text{ cm}^3/\text{g}$. The biggest quantity of adsorbed SO_2 ($13.52 \text{ cm}^3/\text{g}$) is obtained on clay with 5% Ni content, over-carbonized at $T = 450 \text{ °C}$. At the catalyst thermodesorption a small carbon portion was removed from it and sulfur dioxide was extracted with desorption activation energy values less than in comparison with SO_2 desorbing on over-carbonized clay without Ni addition.

It was found out at over-carbonization temperature increasing the desorbed SO_2 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/ γ - Al_2O_3 catalyst, the quantity of absorbed SO_2 increased in 3.5 times.

3.6. Carbonized sorbents on the base of walnut shells (WS) and grape kernels (GP)

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. 12). At $T = 500\text{°C}$ 50% of mass is lost in an hour and, finally, 75% is lost at $T = 950\text{°C}$. 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 3. Phenol sorption by over-carbonized mixture of clay with chrome sludge (1:30).

No	Adsorbent	Phase ratio, g/l	Purification degree, %
1.	Non-over-carbonized chrome sludge	1:10	68,0
2.	Clay	1:10	72,7
3.	Over-carbonized clay	1:10	95,9
4.	Over-carbonized 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

As one can see from the table the specific surface of active carbons on the base of WS increases from 250 to 780 m²/g, the one on the base of GP increases from 200 to 500 m²/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 – absorption analysis it was found out that synthesized active carbons sorb Cu²⁺ and Pb²⁺ ions effectively. The solutions were prepared at metal ion concentration which exceeded maximum allowable concentration in 10 times.

Table 4. Effective surface, porosity and density of over-carbonized samples.

Over-carbonization temperature, °C	Sorbents	Density g/cm ³	Porosity, cm ³ ·g ⁻¹	Specific surface m ² /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

The data on the kinetics of metal absorption by OWS sample are given at figure 12.

As one can see from fig.12 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.

Cracking of propane-butane mixture on cobalt (nickel, palladium) carbonic catalyst has been studied. Carbo-mineral cobalt catalysts are the best.

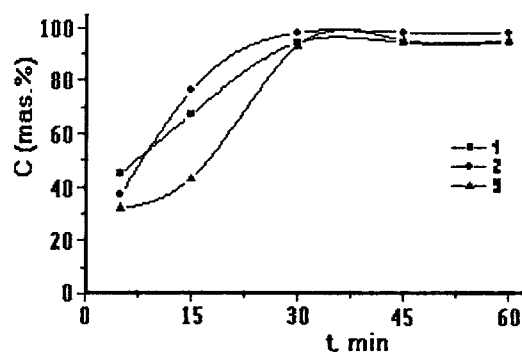


Fig. 10. Metal-carbon catalysts of hydrocarbon cracking. The X-axis - the quantity of sorbed metal ions (% mas). The Y-axis - contact time (min). The curves: 1 - Cu²⁺. 2 - Cd²⁺. 3 - Pb²⁺.

Table 5 shows the results of chromatographic analysis of products of C₃-C₄ hydrocarbon conversion. Fig.13 shows temperature dependencies of olefin and aromatic compound yield.

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

Maximum quantity of olefins is formed at 650 °C; it is 53,5 mass %, gas conversion is 84,8 mass % at 700 °C, odorous compounds is 84,7 mass % at 700 °C.

Fig.13 shows that in temperature interval 500-740 °C it is observed that maximum quantity of olefins is formed at 650°C, 53,5 mass %. In the presence of over-carbonized cobalt catalyst aromatic compound yield is 84,7 mass % at 700 °C. With increasing of temperature aromatic compound yield decreases to 44,9 mass %. The obtained data show that aromatic compound formation has narrow temperature range.

Table 5. Products of C₃-C₄ hydrocarbon conversion on carbo-mineral cobalt catalysts

Products	500°C mass %	600°C mas.%	650°C mas.%	680°C mas.%	700°C mas.%	720°C mas.%	740°C mas.%
H ₂	0,21	0,65	1,32	0,82	1,35	1,57	1,77
CH ₄	1,03	6,5	15,3	13,9	19,5	24,4	21,9
C ₂ H ₆	1,34	16,1	15,7	12,4	12	18,5	25,
C ₂ H ₄	2,26	18,1	31,9	23	24,6	21,5	18,8
C ₃ H ₈	35,5	22,8	10,8	3,52	2,2	1,72	0
C ₃ H ₆	0,90	12,4	17,8	9,54	3,29	1,83	1,53
Iso-C ₄ H ₁₀	9,12	3,37	1,85	0,59	0,19	0	0
C ₄ H ₁₀	34,1	29,4	10,9	2,17	0,72	0,15	0,07
Iso-C ₄ H ₈	0,37	4,15	5,57	2,24	1,56	0,48	1,82
C ₆ H ₆	-	-	7,18	11,7	18,7	19	21
Gas conversio n, %	16,9 3,53	28,3 34,1	60,7 53,5	81,3 34,7	84,8 29,4	79,6 23,8	78 22,1
Σ olefins	-	-	-	-	37,9	57,7	25,5
Composit ion of liquid phase	-	-	-	-	37,8	16,9	12
C ₆ H ₆	-	-	-	-	4,05	2,57	1,24
CH ₃ C ₆ H ₅	-	-	-	-	5,03	3,86	6,21
(CH ₃) ₂ C ₆ H ₅	-	-	-	-	15,2	18,9	55
C ₉₊ , Σ OH	-	-	-	-	84,7	81	44,9

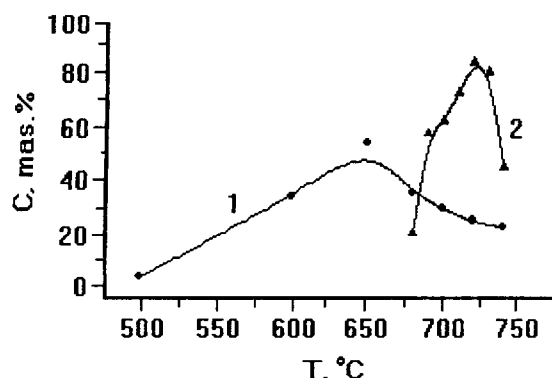


Fig. 11. Temperature dependence of olefin and aromatic compound yield. 1 –olefin yield; 2 – aromatic compound (benzene, toluene, xylene, ethylbenzene) yield.

Table 6. Physico-mechanical characteristics of refractory materials with over-carbonized chrome sludge addition.

Refractory materials	Temperature of inflammation, °C	Temperature of combustion, °C	σ compression, MPa	Porosity, %	Density g/cm ³
	740	1300	9,6	30,1	2,31
	840	1400	22,8	16,8	2,82
	930	1490	28,4	13,5	3,13
	920	1450	16,4	23,0	3,21
	900	1280	13,2	27,0	3,34
«Phurnon-3XP»	830	1500	11	---	---

Table 7. Physico-mechanical parameters of carbon refractory materials on the base of Chilic clay

Addition C + Chrome sludge, %	Temperature of inflammation, °C	Temperature of combustion, K	σ compression, MPa	Porosity, %	Density g/cm ³
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

Improved refractory materials obtaining

Earlier effective non-shaped SVS refractory materials on the base of chrome concentrated were worked out in works of M.B. Ismailov and his colleagues. With the aim of utilization and using of reasonable and cheap raw materials partial substitution of chrome concentrate by chrome sludge was made. Data of obtained refractory materials are presented in tables 6,7.

4. CONCLUSIONS

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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