



Some Problems of the Development of Physics and Chemistry of Carbon Materials

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Abstract

Regularities of formation of nanocarbon materials under catalytic thermal pyrolysis of propane-butane on the Kazakhstan natural clays, chromite and bauxite sludges, containing oxides of the iron sub-group metals, are investigated. Morphology and structures of forming carbon threads with metal particles, fixed at the ends of the threads, are studied and formation of divaricate form of carbon threads – octopus – is found out. The process of carbonization is shown at walnut shells, grape and apricot stones and their cell immobilization for selective adsorption of heavy metal ions and sulfur dioxide. Metal-carbon composites considered as adsorbents for waste treatment, catalysts of cracking C₃-C₄, hydrocarbons and components of refractories with improved characteristics.

Introduction

The report presents the analysis of modern condition of the research of carbon materials and perspectives of its development. The following themes, being developed at Combustion Problems Institute, belong to the most important fields of research:

- problems of soot formation in combustion [1-3];
- carbon nanotubes (CNT) and allied structures [4, 5];
- carbonized materials from vegetative raw materials [6];
- using of CNT as cathode material in chemical sources of current [7].

Recently we have obtained a number of important and interesting results, among them the discovery “Phenomenon of cool-flame low-temperature soot formation” [8].

To solve ecological problems the works on obtaining carbonized materials on the basis of local clays, waste of metal mining industry and agriculture and their using in different applied aspects are important. Obtained adsorption-catalytic systems are applicable for purification of water from organic compounds and heavy metals ions, purification of air from SO₂ and for obtaining improved types of refractories as carriers of catalysts of reactions of hydrocarbon transformation into valuable chemical products: olefins and

aromatic compounds, as well as for benzene elevation. Carbon containing sorbents have a high specific surface and sorption capacity, low cost and they are easily regenerated. Investigations on the properties of nanotubes using gases associated with oil extraction are carried out at the Institute. The study of nanotube characteristics implies creating of new directions of the science of materials.

Last years are characterized by intense development of researches on the formation of carbon nanotubes. It is determined that Fe, Ni, Co and their oxides, as well as these metals alloys, are the most effective catalysts of carbon formation. As the result of catalytic reaction one can see formation of carbon precipitation at dispersed metal particles. This precipitation has specific forms and behavior, which allow considering it as perspective superdispersed systems, being using in various fields of chemistry. For the last years a certain experimental material was gained, which shows development of the directions of successful application of metal-carbon compositions as adsorbents, carriers of catalysts and catalysts of a number of chemical reactions [9].

At present, the laboratories of the Chemical Physics Department and Combustion Problems Institute of al-Farabi Kazakh National University carry out investigations on obtaining carbonized materials on the basis of local clays and wastes of the mining industry: chromite and bauxite sludges, agricultural

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wastes (walnut shells and grape stones) and using them in different applied aspects. The obtained adsorption-catalytic systems find a practical application for purification of oil from sulphur containing compounds, purification of water from organic compounds and heavy metals ions, purification of air from SO_2 and for obtaining the improved types of refractories, as carriers of catalysts of hydrocarbons transformation reactions [1,10].

The structure and morphology of carbon formations

It is possible to obtain a more developed surface with a greater number of active centers than initial samples have by carbonization. Fig. 1 shows electron-microscopic pictures of carbonized chromite slime and clay treated with Co salt. It is seen that formation of carbonaceous deposits results in not only chemical (formation of metal carbide and carry-over of carbide to carbon fibre), but also physical processes – carry-over of particles to carbon mass. Pyrolysis on the surface of the catalyst results in the formation of carbon deposits or the so-called catalytic carbon, the amount of which is 5-10 times more than the initial one. A developed specific surface is related to the morphology of carbon deposits in the form of fibres, tubes and clusters with the diameter of 1500-3000 Å. It should be noted that the growth of carbon fibres (tubes) is of a complicated, sometimes branched character, *i.e.* one metal particle initiates the growth of several carbon fibres in different directions, the so-called “octopus” effect [11].

Simultaneous participation of carbon and metals in the formation of carbon fibres makes it possible to develop new nanostructured composition materials with a complex of various properties.

Mechanochemical encapsulation of quartz particles in metalcarbon films

Mechanochemical treatment of quartz with carbon containing organic compounds in mills of dynamic action and the presence of a small amount of iron in the mixture made it possible to obtain a powder material with ferromagnetic properties which is notable for its high sorption ability hydrocarbons [12].

The structure of the modified quartz particle and its transformation in the process of mechanochemical treatment is clearly shown by the results of elec-

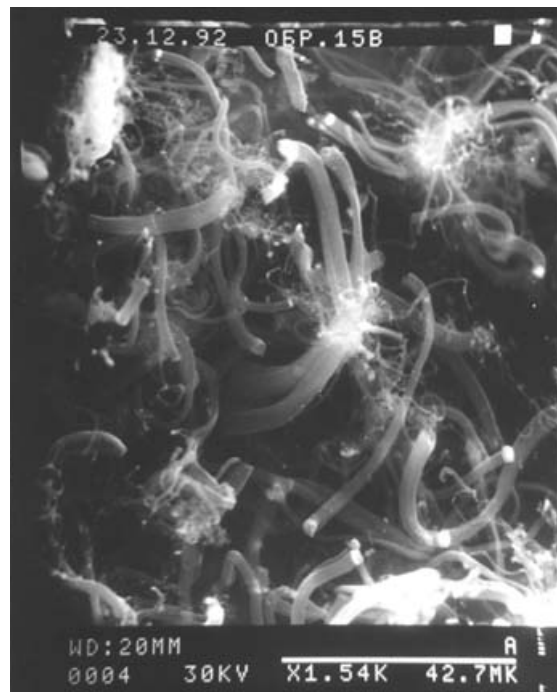


Fig. 1. Electron-microscopic pictures of chrom sludge and Co-catalyst carbonized at $T = 1073 \text{ K}$

tron –microscopic investigations. Particles of standard non-modified quartz of the size from 2 to 10 μm . have strongly marked faces (Fig. 2a). After being milled without modifying organic additives, the surface layer of the particles undergoes partial amorphization followed by intrusion into the surface of ultra disperse iron being ground from the walls of the grinding vessel and balls (Fig. 2b). The use of dispersing organic additives (alcohols, monomers, and polymers) to the quartz being ground in a centrifugal-planetary mill significantly changes the structure of quartz particles. The surface layer is a microporous multifolded formation of different density (Fig. 2c).

The amount of the bound carbon in the modified surface layer of a carbon particle varies depending on the kind of the modifier used (Table 1).

The increase in the carbon amount in the organic modifier being used results in the increase of the amount of carbon being grafted to the particle surface.

When introducing 5% of activated coal, after mechanochemical treatment 3.03% of carbon was found to be in a chemically bound state. When using butanol and polystyrene as modifiers, the amount of carbon was equal to 1.76 and 2.49%, respectively.

Grafting of carbon takes place via active centres of SiO appearing on the surface of the quartz par-

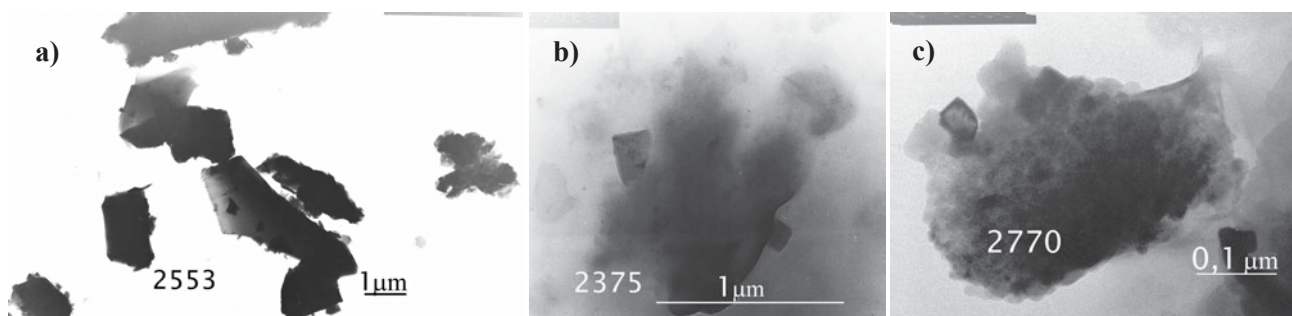


Fig. 2. Electron microscopic pictures of quartz: a) In the initial state, b) after being milled and c) modified by mechanochemical treatment in the presence of carbon containing modifier.

Table 1

The content of iron and carbon in the modified quartz

Material	Content of iron, %	Content of carbon, %
Quartz (SiO ₂)	3.34	0.80
SiO ₂ + C ₂ H ₅ OH (5%)	11.62	1.06
SiO ₂ + C ₄ H ₉ OH (5%)	14.86	1.76
SiO ₂ + C ₂ H ₄ (OH) ₂ (5%)	6.78	1.45
SiO ₂ + C ₃ H ₅ (OH) ₃ (5%)	4.94	1.53
SiO ₂ + activated carbon (5%)	5.62	3.03
SiO ₂ + activated carbon (10%)	5.02	3.48
SiO ₂ + polysterene (5%)	7.08	2.49
SiO ₂ + polysterene (10%)	8.72	2.60

ticle being destructed. In the process of encapsulation of a quartz particle during mechanochemical treatment, an important role is being played by ultra-disperse particles of iron (Table 1) taking part in the process of a polymer compound with a metal in its structure (the formation of metal clusters in a polymer matrix-clusters) resulting in significant changes of the properties of encapsulated quartz particles: electric conductivity, magnetization, sorption ability.

Thus, the structure of the quartz particle surface layer after mechanochemical treatment may be interpreted as containing metalorganic formations in the form of a film enveloping and encapsulating the particle. A material such as that proved to be a good sorbent in the process of purification of water surface from spills of oil and oil products [13] when tested on a pilot unit under laboratory conditions. The quartz powder modified when treated in a planetary-centrifugal mill was scattered onto the surface of an oil spot on water. As a result, coagulation and mag-

netization of the oil film took place. A magnetic transporter removes the oil spot treated by magnetic quartz sorbent from the surface of water completely purifying it.

The amount of sorbent, which is necessary for coagulation and magnetization of the oil to be removed is 10% to the spilled volume of oil. After separation, the sorbent may be used repeatedly; therefore, its reserves in the boat-collector may be considerably limited.

Production of carbongraphite cathodes for chemical sources of current [7]

A coalgraphite layer was grown on metal current taps with the aim to develop an optimal method for production of coalgraphite cathodes for lithium chemical sources of current. The obtained electrodes were tested for the discharge of pure nickel screens, electrodes of fibrous carbon materials and electrodes produced according to conventional technology using polyethylene as a binder. It is shown that the obtained carbonized material is not inferior in its characteristics to a traditional one.

In order to measure electrochemical characteristics of cathodes made according to the proposed method, we created a model of a chemical source of current with a lithium anode and electrolyte containing 1.6 mole/l of lithium chloraluminat in thionylchloride (the electrolyte composition corresponds to that used in commercial samples for this purpose). The electrodes were tested in a galvanostatic regime using two-sided polarization of the cathode, the latter wrapped in a separator of nonwoven glass fibre was placed into a slot cell between two lithium electrodes in the electrolyte, and the electrodes of the unit were tightly compressed. After assembling the unit, under galvanostatic conditions, polarization of the model was carried out by current corresponding

to current density on the electrodes 25 mA/cm^2 . The discharge of the model was carried out till a sharp decrease of the cell voltage. The investigations showed that the above mentioned voltage decrease corresponds to filling carbon material pores with electrolyte reduction products, the main of which is lithium chloride slightly soluble under these conditions.

For comparison, we carried out tests on the discharge of pure (initial) nickel screens, electrodes of fibrous carbon materials using different materials as electrodes made according to conventional technology using polyethylene as a binder. The discharge of the nickel screen at current density of 6 mA/cm^2 showed almost an instant passivation of the electrode by the reaction products that results in a quick decrease of voltage. The discharge of a soot electrode with a polyethylene binder lasted 30 minutes at current density of 12 mA/cm^2 .

The test showed that discharge characteristics of the models of current sources of the lithium-thionylchloride did not practically depend on which of the metals fibrous carbon was deposited. Discharge curves were obtained for samples with coated layers of fibrous carbon in three different regimes (Fig. 3). The mass of the deposited coating varied from 0.01 to 0.05 g. It was shown that the time of the electrode discharge before a sharp decrease of voltage on the cell directly depended on the amount of the coated carbon material and the time of the layer growth. At the discharge in thionylchloride solution with current density of 6 mA/cm^2 the time of discharge reaches 4 minutes.

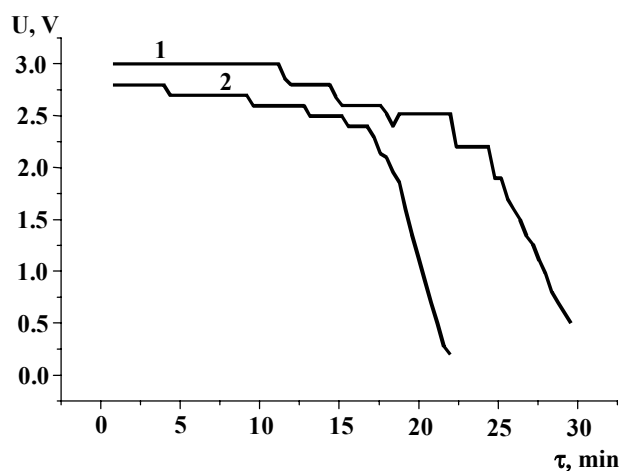


Fig. 3. Discharge characteristic depending on cathode material (obtained by carbonization at 750°C), $i = 20 \text{ mA/cm}^2$: 1 – carbonized iron net; 2 – cathode by standard technology

Multifunctional catalysts of oil hydrofining [10]

Multifunctional catalysts of hydrofining were developed by modifying alumocobaltmolybdenum catalyst with hardened zeolites. Catalysts were prepared by the conventional impregnation method. After moulding, the catalysts had been dried at $393\text{--}420 \text{ K}$ (4 hours) and calcinated at 823 K during 5 hours. Then the catalysts were exposed to the process of carbonization to obtain active forms of carbon as a carrier. Activation of the catalysts was carried out in the process of sulphurizing by free sulphur first at $393\text{--}423 \text{ K}$, at hydrogen pressure $0.7\text{--}1.0 \text{ MPa}$ during 3 hours, then sulphurizing was continued at 473 K , at pressure 2.5 MPa during 2.5–3 hours.

The catalysts were investigated by different physico-chemical methods. Specific surface and porosity were determined by the BET method. The types of adsorbed forms of hydrogen 8 and activation energy were determined with the help of thermo-programmed desorption of hydrogen. The texture of catalysts was determined with the help of electronic microscopy for sight check. The reaction products were analyzed by highly effective gas-liquid chromatography with a capillary column on the chromatograph of “Perkin Elmer” firm. Chromatograms were computed by “Total Chrom Arnel” software. A detailed hydrocarbon analysis was carried out within the framework of “DHA Win” program. The content of sulfur in the samples was determined on X-ray fluorescence analyzer “Oxford Lab-X-3500”.

The activity of catalysts was tested in a laboratory flowing plant in the processes of hydrofining gasoline and diesel fractions of oil at the pressure $2.0\text{--}4.5 \text{ MPa}$, temperature $593\text{--}673 \text{ K}$, volume rate of raw material feed $1\text{--}4 \text{ h}^{-1}$. Characteristics of commercial catalyst GO-70 were taken under equal conditions in order to compare catalytic activity. Butylmercaptan and thiophene diluted in n-decane were used as a model compound. The isomerization activity was tested in the reactions of cracking of hexane and decane. The developed catalysts showed higher indices than commercial catalyst GO-70. With the increase of temperature from 593 to 673 K the degree of hydrodesulphurization increases from 75.3 to 98.2% , and isomerization degree increases from 18.3 to 41.7% . According to the data of the detailed hydrocarbon analysis the estimated octane number increased from 70.83 to 83.48 (Table 2).

Obtaining of active forms of carbon on catalysts

Table 2

Effect of influence of overcarbonized industrial CoMo – catalyst on characteristics of straight-run benzene, concentration of carbon – 10%.

	Octane level	Boiling-point, °C T 10	Concentration		Concentration of S-compound
			Paraffin	(Mass. %) naphthenes	
Initial straight-run benzene (SB)	70.83	88.1	21.42	12.95	0.12
SB after overcarbonized catalyst	83.48	36.06	12.52	16.05	0.001

results in the formation of more highly dispersed systems having correspondingly a higher catalytic activity in hydrofining and hydroisomerization processes. The study of the surface and porosity of catalysts by BET method showed the increase of the specific surface of catalysts from 80 to 240 m²/g. Catalysts, mainly, have pores of the size less than 50 nm. Electron-microscopic investigations showed carbon coated catalysts to be highly disperse. Metal particle size vary within 20-40 nm.

Carbonization of vegetative raw material [6]

The raw material on the basis of treatment of agricultural products belongs to quickly renewable sources and is ecologically more friendly. When carbonizing (pyrolysis in an inert medium) samples of walnut shells (WS), apricot (AS) and grape stones (GS) the main mass loss takes place in the temperatures range 200-500°C. At 500°C during 1 hour, about 50% of mass is lost and, finally, at 950°C the loss reaches approximately 75%.

Specific surface of the samples reaching 830 m²/g was determined by the method of thermal desorption of argon. The electron-microscopic method showed the change of morphology and structure of carbon containing sorbents depending on the temperature and time of carbonization.

The mechanism of sorption of heavy metal ions by carbonized sorbents was stated by physico-chemical methods of analysis. Carbonized sorbents were found to be effective for adsorption of heavy metal ions, organic compounds and sulphur dioxide.

Carbon containing refractories [14]

Introduction of chromite sludge increases the density and mechanical strength in comparison with the refractory "Furnon-3XP", slightly increasing refractoriness. Formation of fibrous carbon and carbides of metals accounts for the improvement of physico-

chemical indices of carbon refractories on the basis of clay and chromite sludge. The obtained refractory materials have a high slag-resistance that allows forecasting their using in metallurgical processes of precious metals production.

Conclusions

Thus, new carbon containing nanostructured materials were synthesized using the activation of natural substances by the method of carbonization. After mechanochemical treatment quartz becomes ferromagnetic. Magnetic permeability of quartz reaches $\mu=30$ depending on the chosen carbon containing modifier and the regime of mechanical treatment. Electroconductivity of the obtained material increases in 2-3 orders.

A coalgraphite layer was grown on metal current taps with the aim to develop an optimal method for production of coalgraphite cathodes for lithium chemical sources of current. The obtained electrodes were tested for the discharge of pure nickel screens, electrodes of fibrous carbon materials and electrodes produced according to conventional technology using polyethylene as a binder. It is shown that the obtained carbonized material is not inferior in its characteristics to a traditional one.

Polyfunctional carbon containing catalysts which may simultaneously carry out hydrofining, hydrodesulphurization and hydroisomerization of petrol and diesel fractions were synthesized. The developed catalysts allow obtaining petrol of low-sulphur content and diesel fuel with improved properties.

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