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THE STRUCTURE UNITY AND PRACTICAL USE OF NATURAL AND SYNTHETIC CARBONIC MATERIALS

S.V. Yefremova

National Center on Complex Processing of Mineral Raw Material of the RK
67 Zhandosov Street, Almaty 050036, Kazakhstan, secretar_rgp@mail.ru

It has been shown the unity of composition, molecular and supermolecular structure of shungite concentrate and silicon-carbon from rice hulls which provides their effective practical use in the same engineering processes as rubber fillers and sorbents.

INTRODUCTION

It is known that solid carbon is widely used in industry and all its varieties have become in deficit. The growing requirements of different branches in carbon materials can be satisfied by using of secondary resources.

There are carboneous wastes with mineral and vegetable nature in Kazakhstan. For example, shungite rock containing carbon mineral named shungite and rice hulls. Shungite rock form rock masses but mostly they are in dumps after complex ore mining and concentration. The rice hulls is a waste of rice processing. It makes up for 20–30% of the mass of rice, i.e. 50,000 tons are generated annually in the Kazakhstan and 150–200 million tons are generated annually in the world.

EXPERIMENTAL

The test objects were the shungite rock and rice hulls of the Republic of Kazakhstan and prepared from them shungite concentrate and silicon-carbon.

The shungite concentrate (ShC) was prepared by shungite rock floatation.

The silicon-carbon ($SiO_2 \cdot C$) was prepared by carbonization of rice hulls in the off-gas atmosphere in the temperature range 650°C at the heating rate 15°C/min within 30 min.

The X-ray phase analysis (XRPA) and high-resolution transmission electron microscopy (TEM) were applied to study the structure of carbonic materials.

The XRPA was performed on a DRON-2 computerized diffractometer with the updated collimation on the filtered CuK_α radiation by the procedure.

The TEM was carried out with a Philips EM 301 transmission electron microscope (the Netherlands) at the accelerating voltage 80 kV within the range of the electron microscopic magnification 13–80 thousand times. For exposure the samples powdered in the agate mortar were laid on the object copper mesh pre-coated with the substrate film of the amorphous carbon and fixed in the microscope object holder.

The EPR spectroscopy was carried with an EPR IRES-1001-2M modernized spectrometer.

The properties of shungite concentrate and silicon-carbon as rubber fillers and the strength properties of rubbers were studied with use of traditional methods.

To prepare carbon sorbents shungite concentrate and silicon-carbon from rice hulls were milled to the grain size of 0.25 to 0.04 mm, then mixed with 35% aqueous solution of sugar at the ratio S:L (g/cm^3) = 1:0.35 and granulated on the plate granulator within 60 min. The grains with size of 2.5 to 0.63 mm were dried at 105 to 110°C within 2 hours and then they were undergone to pyrolysis within 30 min at the temperature of 650°C with concurrent activation by water vapor within 30 min at the temperature of 850 to 900°C.

The study of kinetics of heavy metals, petroleum, precious and rare metals adsorption with the sorbents obtained under static conditions was carried out at the room temperature from the technological solution with their different concentrations at the ratio of the phases sorbent : solution (g/cm^3) = 0.2:100 and also under dynamic conditions, which was performed in the column with diameter of 1 cm filled with sorbents of 2 g in mass. The solutions were carried from the top downward with the velocity of 100 cm^3/hour. Control over the process was exercised both to sorbate content in the parent solutions and in solutions after interaction with the sorbent.

DETAILS OF STUDY

The objective of this study is as follows: the comparative investigation of the structure of natural and synthetic carbonic materials and the determination of the potentialities of their using in the same engineering processes.

Shungite. Shungite rock consists of carbonic material (shungite) and mineral component. The carbon content in natural samples varies from a few percent up to 60%. Mineral part mainly consists of quartzite and different aluminosilicates. Obtained shungite concentrate contained 50% mass of carbon (Table).

Table. Composition and structure characteristics of the carbonic materials

Product	*C*, %	SiO_2, %	d_{002}, Å	L_c, Å	L_a, Å	c_g
ShC	50	30	3.55	23	70	1.15
$SiO_2 \cdot C$	52	32	3.75–3.8	20–26	–	0.45–0.75

We researched structure of shungite carbon of Kazakhstan in matching with different carbonic materials by XRPA. Shungite similarly to coal VI–VII of stages of metamorphism, coke and industrial soot has carbonic turbostratale structure (d_{002} ~3.48 to 3.56 Å, L_c~23 to 26 Å, L_a~70 to 82 Å). The orderliness of graphitic layers of shungite carbon increases with decrease in its content in the rock. Besides graphite-like (carbon) phase in shungite structure, three hydrocarbon phases (polynaphthenic (*d*~4.7 Å) and two oxygen-containing (*d*~8 Å and *d*~18 to 20 Å) phases) were discovered. These hydrocarbon phases turned graphitoid phase as a result of the thermal treatment (Ar, 600°C) of shungite samples [1].

Besides, we researched morphostructures of shungite and industrial soot, coal and coke by method of transmission electron microscopy. Morphostructure of shungite is submitted by congestions of dendrite and isometric shapes (Fig. 1*a*). It is known that soot has a chain structure. We found that dendrite structure of shungite is similar to the chain structure of soot. Both shungite and soot morphostructures are formed by spherical particles. But shungite particles (20 to 30 nm) are 2–3 times lesser than particles of soot (40 to 100 nm) and formed by fine particles of the size of 1.5 to 2.5 nm. And in shungite the porous formations were found in which one the pore size reaches 5 nm and the size of particles reaches 4 nm. But the resemblance between a pine-tree supermolecular structure of shungite and supermolecular structure of coke was not found. So, by its structure Kazakhstan shungite is similar to disordered forms of industrial soot [2].

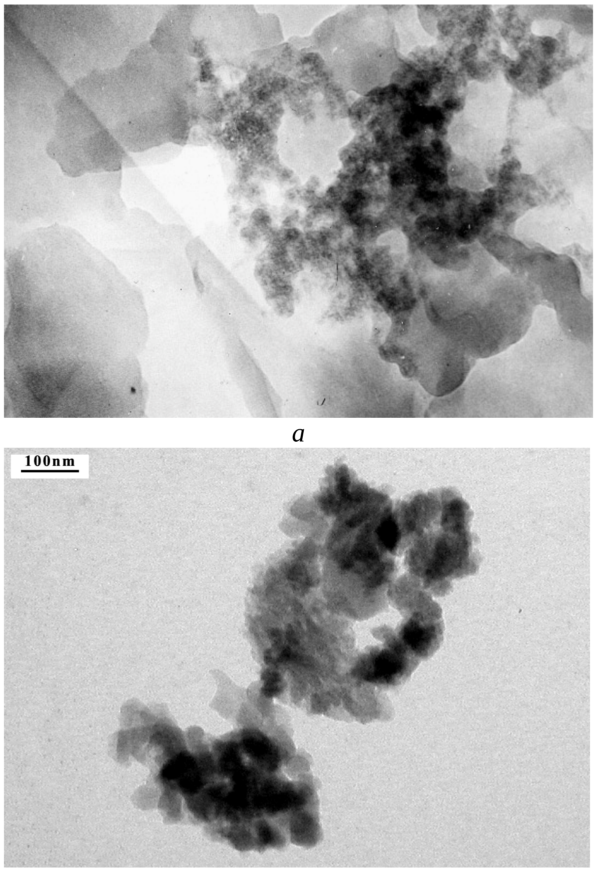

Fig. 1. Supermolecular structures of the shungite concentrate (*a*) and silicon-carbon from the rice hulls (*b*)

Shungite particles being formed by graphitoid layers with 'holes', the former is a cluster-containing material with energy heterogeneous surface. The sites of the greatest accumulation of graphitoid layers structure defects are the most energy saturated. The great quality of excess energy accumulates on unbound electrons localized on defects. It is confirmed by the data of EPR spectroscopy [3]: there is an intense signal showing the presence of the great quality (10^{19} spin/g) of unbound electrons in the shungite particles in the EPR spectrum of material.

Silicon-carbon from rice hulls. The rice hulls contains a great amount of silica (14%) unlike other vegetable wastes. Therefore the product of thermal processing of rice hulls called as silicon-carbon ($SiO_2 \cdot C$) is a composite containing 52% of carbon and 32% of silica as it is shown in Table.

By X-ray phase analysis method, the presence of the graphite-like (carbon) phase was detected in the composition (d_{002} = 3.75 to 3.80 Å) and two hydrocarbon phases: polynaphthenic phase (d ~ 4.7 Å) and phase with an unidentified (failing this hydrocarbon phase in clear form) structure (d ~ 8.0 Å).

The nanostructure of the carbon phase of the silicon-carbon is presented by crystallites with the cross sectional dimension L_{002} ~20 to 26 Å which are composed as analogous graphite grids with spacing C–C of 1.42 Å. As compared to the graphite structure, it is less perfect although with the temperature rise during pyrolysis in the temperature range of 500 to 1000°C, some insignificant increase in graphitization level (c_g) was observed (from 0.45 to 0.75). In this case, the volume of the graphite-like phase increases (from 45 to 100%). After treatment of the initial sample at 1000°C, the X-ray phase analysis records transformation of the amorphous silicon dioxide to crystobalite [4, 5].

Both silicon-carbon and shungite morphostructures of are formed by spherical semi-translucent nanoparticles and isomorphous formations (Fig. 1*b*).

By data of EPR spectroscopy, the concentration of free-radical states (N) in the silicon-carbon varies depending on carbonization temperature (Fig. 2) [6].

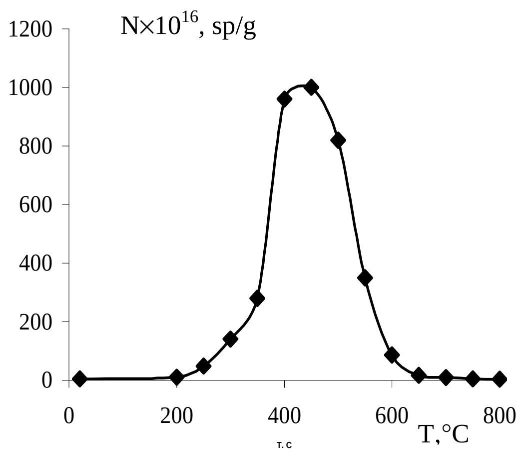

Fig. 2. Changes in concentration of free radicals in silicon-carbon with temperature rice

The data presented show that the test materials have no significant difference in their molecular structures and they have similar supermolecular structures. They are composites formed by carbon and silica nanoparticles. The unity of composition and molecular and supermolecular structures of investigated shungite concentrate and silicon-carbon from the rice hulls causes likeness of their physical and chemical properties and makes for their effective practical use in the same engineering processes.

Practical use. The shungite concentrate and silicon-carbon from the rice hulls were tested in a view of use as rubber fillers and sorbents in various engineering processes.

It has been shown that test fillers improve the rubber strength properties and can be used as substitutes of carbon black. The efficiency of their use as rubber fillers has been confirmed by results of their tests in the "Rubber" (Issik) company Ltd [7].

The sorbents was prepared from shungite concentrate and silicon-carbon of rice hulls and their sorptive properties were determined. They are used in various sorptive processes.

A principal opportunity of using of sorbents from shungite concentrate as sorbents for water (from heavy metal ions Pb^{2+}, Zn^{2+}, Cd^{2+}, and petroleum) purification has been found. It was shown that modification of shungite sorbent surface by immobilization of microorganisms cells active in processes of heavy metals ions accumulation and petroleum oxidation increases its sorption capacity to these pollutants [8].

The prospect of using of the sorbent from silicon-carbon for gold and rhenium recovery from productive solutions was found [9, 10].

CONCLUSION

The data presented show that the shungite concentrate and silicon-carbon of rice hulls as natural and synthetic carbonic materials respectively have similar molecular and supermolecular structures and physical-chemical properties. It opens up new potentialities for producing a number of materials of different purpose on the basis of them.

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Структурна єдність та практичне використання природних і синтетичних вуглецевих матеріалів

С.В. Єфремова

Національний центр із комплексної переробки мінеральної сировини РК
вул. Жандосова, 67, Алмати 050036, Казахстан, secretar_rgp@mail.ru

Показано єдність складу, молекулярної та надмолекулярної структури шунгітового концентрату та синтетичного кремневуглецю з рисового лушпиння, що забезпечує можливість їхнього використання в одних і тих самих технологічних процесах як наповнювачів гуми та сорбентів різного призначення.

Структурное единство и практическое использование природных и синтетических углеродных материалов

С.В. Ефремова

Национальный центр по комплексной переработке минерального сырья РК
ул. Жандосова, 67, Алматы 050036, Казахстан, secretar_rgp@mail.ru

Показано единство состава, молекулярной и надмолекулярной структуры шунгитового концентрата и синтетического кремнеуглерода из рисовой шелухи, обеспечивающее возможность их использования в одних и тех же технологических процессах в качестве наполнителей резин и сорбентов различного назначения.