

CHEMICAL REACTIONS ON THE SURFACE OF CARBON

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Introduction

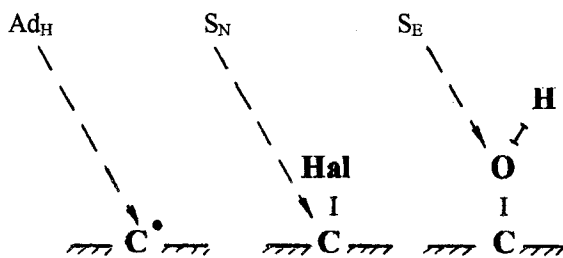
There is a great interest to the chemical transformation with participation of surface centers of diamond and graphite at present time. It is connected with carbon materials perspectives in manufacturing of new generation of high quality composites with different types of matrixes. The diamonds and graphites with uniform layer of chemically inoculated groups with different electronic structure are interesting also in theoretical aspect.

Experimental

Monocrystals and powders natural and synthetic diamonds and graphites was used.

The types of reactions on the surface of carbon

The chemisorption transformations with participation of diamonds and graphites surface centers can be related to homolytical and heterolytical processes. Among studied reactions with participation of surface functional groups of diamond and graphite the reactions with participation of radicals-homolytical processes of combination (Ad_H) and heterolytical-reactions of nucleophilic and electrophilic substitution (S_N , S_E) were determined. The possible types of these transformations with participation of carbon surface centers may be presented by the following scheme:



Reactions with attacks to carbon atoms

A. Homolytical combination (Ad_H)

Real surface of diamond and graphite (crystals, powders) contains oxyfunctional groups identified by methods chemical analyses and X-ray photoelectron

spectroscopy, as C-O, C-OH, -COOH [1]. The thermodesorption of these groups in the interval 20-1000°C is characterized by giving off CO_2 and CO with maximums at 500-600°C for diamond and at 400; 600; 1000°C for graphite. Under condition of vacuum or inert gas current during thermodesorption of CO_2 and CO, the obtaining of surface carbon σ -radicals of diamond was proved by method of ESR [2]. Diamond paramagnetism is changing in accordance with the changing of thermodesorptial spectras, maximum quantity of obtained radicals (\dot{C}) up to 2.5 $\mu\text{mol}/\text{m}^2$. The following treatment of the diamond and graphite by O_2 , Cl_2 or Br_2 leads to ruin of the radicals, resulting in new functional groups (C-O, C-Hal) formation on the surface. The quantity of these combination groups is a function of the synthesis temperature and correlates with the thermodesorption curves and the date of ESR (Fig. 1)

B. Heterolytical nucleophilic substitution (S_N)

The surface compounds containing the groups C-Gr (Gr: -H, $-CH_n$, -OH, -N) were obtained by substitution of the haloid centers of diamond and graphite in reactions with H_2 , CH_4 , H_2O , and NH_3 . The kinetic isotherms of these reactions are described by equation

$$\theta^n = a \ln(t) + c$$

for unhomogeneous surface with activation energy changing in the interval from 29kJ/mol (at $\theta \rightarrow 0$) to 71 kJ/mol (at $\theta = 0.5$). The diagram of quantitative substitution of groups versus temperature is shown at Fig. 2.

The reactions with attacks to oxygen atom of oxyfunctional groups

Complex halogenides elements or elementorganic compounds (III- YI groups) synthesis in reactions of electrophilic substitution proton (S_E) in diamond and graphites surface layer oxyfunctional groups C-OH, -COOH permits to carry out local modification of the surface. The kinetics of that type reactions is described by equation

$$-\ln(1-\theta) = kt$$

for the model of homogeneous surface. The chemisorption of these reagents takes place under milder conditions starting with room temperature, the activation energy does not exceed 10-20 kJ/mol in range of 20-200°C. The value of element-haloid complex chemisorption depends on the amount of proton containing oxyfunctional groups and changes in the range of 0.1-5.0 $\mu\text{mol}/\text{m}^2$. The composition, nature of bond and energy characteristics of obtained compounds are shown in the table.

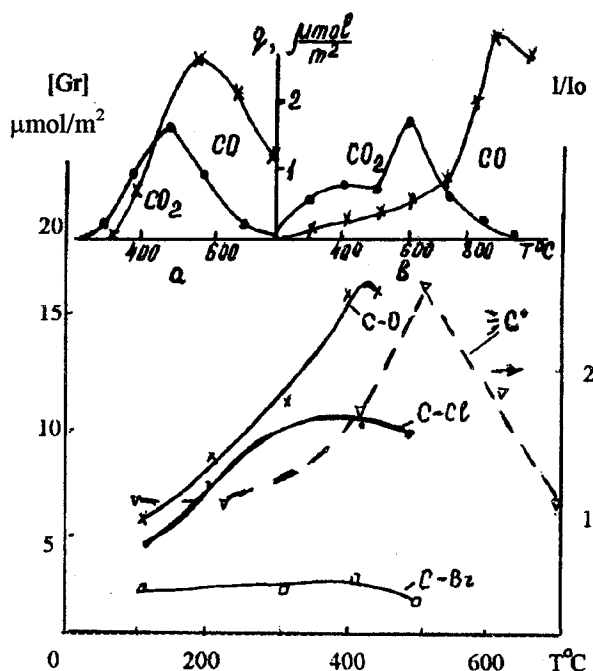


Figure 1. Relative intensity ESR (I/I_0) and concentration $[Gr]$ of groups, the date of thermodesorbition (a) diamond and (b) graphite

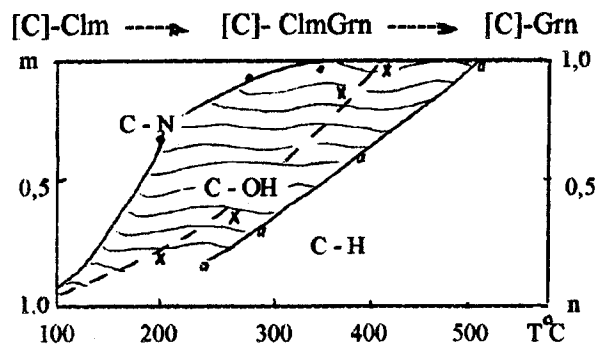


Figure 1. The reaction of substitution (S_N) diagram.

Table. Composition of the monolayer covering after surface modification

Functional group	Reacting substance	Product	X-ray photoelectron spectrum		
			Line	E_b , eV	$[Gr]/[C]1O^2$
diamond					
$\equiv C^\bullet$	O_2	C-O	01s	532.0	10.0
	Cl_2	C-Cl	C12p	199.4	2.5
	Br_2	C-Br	Br3p	184.8	0.7
C-Hal	H_2	C-H		-	-
	H_2O	C-OH	01s	532.0	3.0
	NH_3	C-N	N1s	399.0	2.5
C-OH -COOH	Al_2Br_6	C-O-Al	Al2p	73.6	1.9
	$TiCl_4$	C-O-Ti	Ti2p	458.2	1.9
	$VOCl_3$	C-O-V	V2p	516.8	2.8
	$MoCl_5$	C-O-Mo	Mo3d	231.9	0.2
	WF_6	C-O-W	W4d	246.7	0.6
graphite					
$\equiv C^\bullet$ ⊥	O_2	C-O	01s	532.3	5.0
	Cl_2	C-Cl	C12p	199.9	2.5
	Cl_2	none	-	-	-
		C-Cl	C12p	199.9	8.6
C-OH	Al_2Br_6	C-O-Al	Al2p	74.4	3.5
	$TiCl_4$	C-O-Ti	Ti2p	459.0	0.3
	$VOCl_3$	C-O-V	V2p	517.2	0.2
	WF_6	C-O-W	W4d	247.9	0.6

References

1. Lukjanov, I.M., Smirnov, E.P., *Sov.J.Theor. and experimental chem.*, 1989, 4, 490.
2. Abyzov, A.M., Smirnov, E.P., *Sov.J.Chem. Phys.*, 1992, 7, 1002.