ADSORPTION ON MODIFIED SYNTHETIC DIAMOND POWDERS

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Introduction

Chemical treatment of natural and synthetic diamond surfaces with chlorine, fluorine, and hydrogen are used for modification of the physical and chemical properties of the diamond surface. Such treatments are a subject of interest in phase-transfer catalysis, mechanical engineering, the electronics industry, etc. The successful selection and use of chemical modification methods requires a full understanding of the relative stability and interactions on different modifications of diamond surfaces. With this objective, physical, physical-chemical, and molecular mechanics methods have been used.

Experimental

As grown synthetic diamonds have been thermochemically treated with oxygen, chlorine, fluorine and hydrogen by using a hydrogen generator. Before and after synthetic diamond surface thermo-chemical modifications, specific magnetic susceptibility, χ, tangent of dielectric losses angle, tgδ, and free energy for water vapour saturation, ΔG_s have been measured. To determine the quantity and density of unsaturated broken chemical bonds ESR measurements have been carried out.

Isotherms for adsorption of fatty acid C_7 - C_9, kerosene, and decane from water emulsion at 293K and nitrogen at 77K on a surface of diamond powders, synthesized under different thermobaric conditions, in a wide range of fraction intervals have been obtained, and sorptive characteristics determined.

Considering the carbon atoms clusters with diamond-like structure as a supermolecule one can employ the molecular mechanics methods for comparing the energies of layers on diamond surface with different arrangement of chemisorbed functional groups and atoms. Though the molecular mechanics methods have been developed for conformation investigations of molecules, being applied for systems with the same atomic content they give reliable results, because one can consider the different arrangements of chemisorbed atoms as a limiting case for conformation changes. Having considered all possible surface filling cases for a given atomic set, one can to draw conclusions about most preferable ones.

For example, a case has been considered where a cluster of 38 carbon atoms lying in four parallel to diamond basal plane (111) layers, giving 12 active sites on its surface in which every pair combination of -H, -F, -Cl atoms and -OH group have been symmetrically placed. 80 atoms, 97 bonds, 228 angles, 495 torsions, and up to 2000 most significant Van der Waals interactions have been taken into account, when full geometry optimization procedure having been performed. Two different force field parameters sets supported by ATOM and ALCHEMY programs have been used for total energy calculations.

Results and dIscussion

One can observe II and IV type adsorption isotherms, so BET-theory analysis has been used. Study of fatty acid adsorption is of great importance due to its role in extraction process of diamond powders from reaction mixture.

The investigations carried out have shown that metal catalyst impurities are concentrated mainly in near-surface layers. The most significant changes are caused by

chlorination treatment when number and density of metal admixtures are decreased while quantity of broken chemical bonds are increased up to 30% according to ESR measurement. As a result of hydrogen thermochemical treatment, the number and density of metal impurities do not change but the quantity of broken chemical bonds are decreased significantly. The data for synthetic diamond surface thermochemical treatments give the base for considering synthetic diamond surface as a surface with structure obtained as a result of chemical interaction of diamond carbons and metal impurities with reagents during the diamonds extraction and purification.

The thermochemical chlorination and hydrogenation of synthetic diamonds surface also have influence on its sorptive peculiarities due to changes of its hydrophilic/hydrophobic rate. The chlorinatied species demonstrate hydrophilic behaviour, while hydrogenated ones act vice versa. It makes possible the use of modified synthetic diamonds as carriers for different variants of chromatography, especially for phase-reversed one.

Micropowders

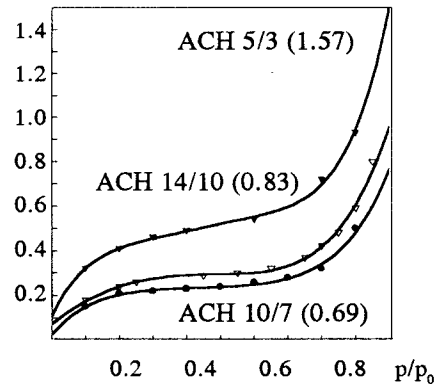

Figure 1 - Isotherm for adsorption of nitrogen at 77K on synthetic diamonds (S_{BET} in m^2/g)

Comparison of calculated data for structures with the same atomic contents shows the preference of fluorization above hydrogenation and chlorination treatment of diamond basal planes covered by -OH groups in accordance with experimental observations. The different surface defects influence on diamond surface filling may be estimated by considering non-plane model clusters of diamond surface.

TABLE 1 - Sorption parameters of different types of diamond powders

Powder type	Fraction, mkm	Specific surface, m/g	Monolayer volume, ml/g	Pore volume, ml/g	Latent heat, J/g	BET equation constant
AC32	80/63	0.048	0.011	0.015	11.64	202.6
AC32*	80/63	0.076	0.017	0.025	-2.94	46.9
ACM	60/40	0.100	0.023	0.140	-	-
ACM**	60/40	3.370	0.770	3.000	11.28	2.8
ACM	40/28	0.160	0.037	0.260	23.70	140.0
ACM**	40/28	12.510	2.900	10.700	29.00	2.5
ACH	14/10	0.709	0.163	0.915	33.77	62.9
ACH	10/7	0.675	0.155	0.761	56.63	318.7
ACH	5/3	1.535	0.353	1.438	47.30	73.7
ACM	7/5	0.94	0.216	0.950	32.74	44.2
ACM†	7/5	36.50	8.380	29.770	48.70	3.4
ACMK	5/3	1.434	0.329	1.318	39.82	47.1
ACBM	7/0	28.175	6.472	31.10	103.37	190.9
UDD	-	148.5	34.1	6.78	-	-245.1

* - CrO_3 treated, ** - non-standard conditions of synthesis, † - chlorinated species