

SURFACE PROPERTIES OF CARBON-MINERAL ADSORBENTS AS EXAMINED BY ^1H NMR SPECTROSCOPY

R.Leboda, V.V.Turov, J.Skubiszewska-Zięba* and V.I.Bogillo*

**Faculty of Chemistry, Maria Curie-Skłodowska University
20031 Lublin, Poland*

*Institute of Surface Chemistry, National Academy of Science,
Pr.Nauki 31, 252022 Kiev, Ukraine*

Introduction

The free surface energy of the solids and radial function of free energy change of liquid/solid interface are a most important characteristics determining their adsorption ability in different media. The characteristics of the hydrated shell layer on the adsorbent particles may be evaluated on the basis of the ^1H NMR signal intensity for non-frozen liquid in the process of freezing of the aqueous suspension under investigation.

The water at the interface of the adsorbents freezes at the temperatures $T < 273$ K in the case, when free energy of the molecules in adsorbed state becomes equal to that for the molecules in the bulk of ice. As the free energies are tabulated in a wide temperature range, the dependence of the non-freezing water concentration on the temperature can be easily transformed into plot of water free energy change on the distance of the adsorbed water molecules towards the surface plane. The free energy of water in interface layer (G) can be determined on the basis of temperature dependence of the free energy of ice (G_i) [1]. The suggestions that water freezes at the interface only in the case when $G = G_i$ [2-4] and the $\Delta G = G_o - G$ difference determines a decrease in the free energy of the water molecules due to adsorption to be accepted, where G_o is the free energy of ice formation at 273 K. The capillary phenomena on the solid surface are not observed for adsorbents placed into liquid media and the function $\Delta G = f(C_{\text{H}_2\text{O}})$ determines the radial function of free energy change in the water/solid interface. The overall free surface energy of the adsorbed water film (ΔG_Σ) can be determined by integration or, approximately, by

summing of the function $K \sum \Delta G(i) \cdot i$, where K is a conversion factor and $\Delta G(i)$ is the average value of water free energy in i th monolayer. The summation should be performed over all number of statistical water monolayers in interface layer from $i = 1$ to $i = D_{\text{max}}$, where D_{max} is the maximal value of thickness of nonfreezing water layer. The $\Delta G(1)$ value corresponds to average value of water free energy in the immediate first monolayer with respect to surface and it reflects the action of short-range van der Waals, polar and hydrophobic surface forces on the spatial structure of interface water, whereas G_Σ and D_{max} quantities characterize the action of long-range structural forces in this system.

Experimental

Above approach was used for study of the surface characteristics of dispersed carbonized silicas (CS1 and CS2) prepared by pyrolysis of methylene chloride on the dehydrated surface of non-porous pyrogenic silica (Aerosil 300) as well as of mesoporous carbonized silicas synthesized by pyrolysis of acetylacetone on the silica gel surface (CS3, CS4 and CS5). The properties of mesoporous carbonized silica gel containing Zn and Ti oxides on the surface (CS6 and CS7) have been investigated in the same way. The latest mixed silicas were prepared by thermolysis of Zn and Ti acetylacetonates on the silica gel surface. From the spectral data it follows that water is not sorbed on the basic graphite planes of carbon part of the surface of carbonized silicas. The adsorbate is largely concentrated near oxygen-containing sites which are present both on silica and carbon parts.

Table 1 Characteristics of the investigated adsorbents.

Adsorbent	S (m ² /g)	C _c (% w/w)	KΔG(1) (mJ/m ²)	ΔG _Σ (mJ/m ²)	D _{max} (nm)
A 300	280	0	67	150	3.0
CS1	224	0.5	54	920	13.5
CS2	108	40	58	294	3.0
SG	368	0	59	160	1.5
CS3	359	4.0	67	26	0.6
CS4	303	9.1	47	91	2.5
CS5	281	14.5	61	61	1.2
CS6 (12% ZnO)	212	4.0	59	204	2.6
CS7 (12% TiO ₂)	192	4.0	59	208	2.4

Results

The specific adsorption surface area (S), percentage of carbon in the samples (C_c), ΔG(1), ΔG_Σ and D_{max} values for all parent and mixed oxides are presented in Table 1. From these data it follows that in the case of nonporous carbonized silicas the increase of carbon content on the surface leads to enhancement of the overall free surface energy of adsorbed waterfilm and maximal thickness of the nonfreezing water layer. This effect is most pronounced for CS1 sample containing minor percentage of carbon. The G_Σ value for mesoporous carbonized silicas irrespective of the carbon content tends to diminish as compared with parent silica gel and it increases at modification of the carbonized surface by Zn and Ti oxides.

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References

1. V.M.Gunko, V.I.Zarko, V.V.Turov, E.V.Voronin, V.A. Tischenko, A.A.Chuiko, Langmuir. 11, 2115 (1995).
2. V.V.Turov, V.I.Bogillo and R.Leboda, Ext.Abstr. EUROFILLERS 95, Mulhouse, France, 131, (1995).
3. V.V.Turov, R.Leboda, V.I.Bogillo, J.Skubiszewska-Zięba, Langmuir. 13, 1237 (1997).
4. V.V.Turov, R.Leboda, V.I.Bogillo, J.Skubiszewska-Zięba, Langmuir. 11, 931 (1995).