**Lecture 5.** Surface properties of nanoparticles. Adsorption.

Adsorption is an increase of substance concentration at the interface (phases F1 and F2), (Fig. 1).

The substances adsorbed on the surface are called as adsorbate (Fig. 1,1), surface adsorbing the substances is an adsorbent (Fig. 1, 2). Adsorption is a spontaneous process. Excessive adsorption or Gibbs adsorption (Г) shows the change of adsorbate concentration as a result of adsorption. According to the fundamental Gibbs adsorption equation a spontaneous decrease of the surface tension σ occurs due to the chemical potential µ change; for a one-component system this dependence is defined as follows:

$Г= - dσ/ dµ$ (1)

The chemical potential is a factor of the intensity of any physicochemical process. The process proceeds spontaneously from a larger chemical potential to a smaller one. The sign «-» shows the surface tension decreasing as a result of adsorption. The value of excess Gibbs adsorption is determined by the mass of the adsorbent the per unit of the interface (kg/m2). Due to the great specific surface area and the excess surface energy, nanoparticles can significantly adsorb.



Figure 1 – Scheme of the adsorption process: a) initial moment; b) the equilibrium state

Adsorption on the surface nanoparticles has its own characteristics which are determined by the size effect, the crystal structure of nanoparticle surface and the predominance of chemical adsorption over the physical one. The size effect is determined by the number of adsorbed particles n0 with density on the crystalline surfaces which equals to:

*na = n0 ( - Ea / KT),* (1)

where, *Ea* is the adsorption energy or adsorption potential, *n0* density of atoms on the nanoparticle surface.

The adsorption potential characterizes the reversible isothermal work of the adsorption forces and equals to:

*Ea = RT ln p/ps*, (2)

where, *p* is the pressure of an adsorbent over the surface of the adsorbent, *ps* is the pressure corresponding to the condensation of the adsorbent to form a liquid on the surface of the adsorbent.

So, for nanoparticle of the diamond, the adsorption potential, depending on size of nanoparticles, changes as shown in Table 1:

Table 1

|  |  |  |
| --- | --- | --- |
| Particle size, nm | 130 | 8 |
| Adsorption potential, J/g | 141.2 | 384 |

The particle size reduces by 16.2 times and the adsorption potential increases by 27 times. The increase of the adsorption potential with decreasing of particle size is explained by the size effect, by the increase of the fraction of atoms on the surface as compared to their amount in the bulk. The adsorption energy is directly related to the interaction of adsorbate with the adsorbent. This relationship can be observed at the adsorption of hydrogen on nanoparticles of titanium alloys (TiNi, TiFe, TiPb). Adsorption of hydrogen on the surface of titanium alloys is characterized by the following parameters (Table 2):

Table 2

|  |  |  |  |
| --- | --- | --- | --- |
| Alloys | Adsorption energy, EW | Binding energy, EW | Adsorption layer thickness, nm |
| TiNi | -0.88 | -3.25 | 0.046 |
| TiFe | -0.75 | -3.12 | 0.048 |
| TiPb | -0.34 | -2.72 | 0.052 |

As follows from the data presented in Table 9 the adsorption of hydrogen is preferable for TiNi, TiFe compared to TiPb, where the adsorption energy is proportional to the binding energy between the adsorbent and the adsorbent. The presence of such bond characterizes chemical adsorption (chemisorptions). For nanoparticles, as for all adsorbents, is characterized by physical and chemical adsorption. Physical adsorption proceeds due to intermolecular interaction. When physical adsorption is realized the atoms are mobile and can "roll" over the surface at a distance exceeding the interatomic distances. A distinctive feature of chemical adsorption, or chemisorption, is the irreversibility of the process and a significant thermal effect. Chemisorption on the surface of nanoparticles is determined by the size effect (Lecture 4), the structural properties of nanoparticle, including the crystalline nature. The ability of nanomaterial to realize chemisorption is much higher than that for macroscopic bodies. In addition to the size effect, adsorption is affected by the structural and electronic properties of nanoparticles. These factors are closely interrelated and their effect on adsorption is sometimes difficult to assess.

In addition, there are substantial number of unsaturated atoms on nanoparticle surface which capable to form chemical bonds. The nature of the unusual adsorption capacity of nanomaterials can be considered on the example of some chemical interactions. Research the adsorption of CO on Pb, Cu, Ni nanoparticle deposited on graphite showed that the transition of metal-dielectric is accompanied by the enhancement of the CO-Me bond. Nanoparticles of Pb and Ni (with size less than 3 nm) exhibit high reactivity with respect to O2 and H2S. In this range of particle sizes, the metal properties of palladium and nickel are weakened.

Direct evidence of the electronic effect of adsorption was obtained by adsorption of gases on single crystals of metal, coated by monolayer palladium. The electronic structure of palladium promotes the formation of chemisorption bonds. Adsorption depends on the structure of the metallic nanoparticles. Effective chemisorption is observed when oxygen is adsorbed on platinum nanocrystals consisting of grains and transition sites. Oxygen molecules are firmly associated with the transition sites due to chemisorption between the crystal faces. The ratio between the transition sites is determined by the nanocrystal sizes. If the size is less than 10 nm, the transition sites predominate, and when the size increases to 60 nm, the faces predominate.

The dependence of adsorption on the concentration is characterized by adsorption isotherms which show the increase of adsorption with increasing of adsorbate concentration. Adsorption can be monomolecular when monolayer of adsorbate is formed on the surface of adsorbent, and adsorption is polymolecular one, when two or more monolayer of adsorbed substances is formed on adsorbent surface.

Adsorption of polymers on nanoscale objects has a number of features (Fig. 16). At horizontal adsorption (Fig. 16, a), a strong bondings of polymer with the surface of nanoparticle dispersed phase is formed, and the adsorbed layer has molecular dimensions. At vertical adsorption (Fig. 16, b), a bulk layer weakly interacted with the adsorbent is formed, and the polymer molecules can easily lose their bond with the adsorbent (desorption process). "Loops" (Fig. 2, c) correspond to an intermediate variant of the adsorption interaction.



Figure 2 – Various forms of the adsorption state of polymers on nanoscale surfaces: a-horizontal, b-vertical, in-with the formation of "loops"

Absorption processes can change the nanoparticle surface properties: impart them hydrophobicity or hydrophilicity, electrical conductivity, magnetic susceptibility, etc.

Thus, due to the adsorption of water vapor, the surface property of diamond particles can vary from hydrophobic modification to hydrophilic one. The presence of a large number of fine pores (their size can vary from 0.4 to 0.7 nm) imparts to nanoporous materials a considerable adsorption capacity. The specific surface of such adsorbents can reach 1.10 m/kg. High activity of nanoporous materials is not explained by only a simple increase of the specific surface. The relatively large number of atoms on the surface and on the near-surface layers with high curvature can radically change the adsorption capabilities of the catalyst. By means of nanoparticles the ion-exchange adsorption can occur. Ion-exchange adsorption is a reversible process of equivalent exchange by ions between electrolyte solutions and solids called as an ionite.

Cation-exchange and anion-exchange adsorption are distinguished. The scheme of cation-exchange adsorption can be given as follows:

Cat1 +[…]-  + Cat2+ Cat2+[…]-  + Cat1 +

ion exchanger solution ion exchanger solution

Intensive ion-exchange adsorption is observed on crystalline of nanoparticles because the process occurs not only on the crystal surface, but also in the crystal cavity.

The relative large intergranular distance (0.7-0.8 nm) makes it possible to carry out the cation exchange on a large surface.

Adsorption processes are the basis of any catalysis, that is, changes (mainly increase) of the rate of chemical reactions. Catalysis occurs through several stages: the adsorption of reacting substances by nanoparticles, the migration of adsorbed molecules into the interior of the catalyst, the formation and desorption of reaction products. Mainly, adsorption processes determine the rate of catalysis.

The process of catalytic oxidation from CO to CO2 has importance. In turn, the oxidation process is determined by the rate of adsorption.

The high catalytic activity is characteristic of nanoparticles. Electronic and geometric effects are explained by small particle sizes. The number of atoms in composition of nanoparticles is small, the distance between the energy levels is:

*δ = Ef /N*, (3)

where Ef is the Fermi energy (the energy value below that all states of the system obey to the quantum statistics, in one state there cannot be more than one particle); N is the number of atoms on the surface of particles, which characterizes the size effect.

Using formula (14), it is possible to estimate the size of nanoparticles used as catalysts.

Nanoparticles are used as an adsorbent for water purification. The adsorption capacity of nanoparticles of aluminium for heavy metals is 10-80 mg per gram of adsorbent, for halogens 10-45 mg per gram of absorbent, for organic substances up to 150 mg per gram of absorbent, for oil emulsions up to 250 mg per gram of absorbent. The degree of extraction of microorganisms is 80-99 %, and degree of extraction of petroleum products is 99 %.

Adsorption by means of nanoparticles significantly improves the efficiency of catalysis. Most catalysts are nanosystems. In case of heterogeneous catalysis, the active substance is mounted on a carrier in the form of nanoparticles to increase the specific surface area of the catalyst and the efficiency of catalysis. In homogeneous catalysis, the molecules of the active substance are nanosized. They can be sorbed on the nanoparticles and desorbed slowly.

**Revision question:**

1. What is the adsorption?
2. How does the adsorption process proceed?
3. Describe the Gibbs equation.
4. Give the examples of size effect with respect to adsorption.
5. What is the difference between chemisorption and physical adsorption?
6. What peculiarities of nanoparticle adsorption do you know?
7. What do monomolecular and polymolecular adsorption mean?
8. What do you know about polymer adsorption?
9. What are features of ion exchange by nanoparticles?
10. Why does the nanoparticle size influence on catalytical processes?