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CHEMICAL REACTIONS IN NANOPARTICLES

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The problems related to the influence of the nanoparticle size on the chemical reaction proceeding in it are investigated theoretically. As an example, the reaction of oxidation of a nanosized silicon particle is considered.

Keywords: *nanoparticle, chemical reaction, size effect.*

It is known that the activation energies for a number of processes occurring in nanoparticles can differ from the activation energies for the same processes in a bulk phase. In particular, the activation energy for the diffusion of atoms in nanoparticles decreases with size of the nanoparticles [1]. A change in the mobility of atoms (molecules) with change in the size of nanoparticles can also affect other processes connected with the mobility of atoms, for example, the coalescence of nanoparticles, the course of chemical reactions in them, etc. Below some problems related to the influence of the size of nanoparticles on the rate of chemical reaction in them are considered with the aid of the example of oxidation of silicon nanoparticles.

The influence of the size of nanoparticles on the mobility of atoms in the particles is connected with the fact that the energy of formation of vacancies in nanosized particles decreases with the size of the particles [2, 3]. This leads to an increase in the concentration of vacancies in a small particles (c_{p}) in comparison with the concentration in a massive sample (c_∞). According to [3], the compression for c_{p} can be written as

$$c_{\text{p}} = c_\infty \exp\left(\frac{6\sigma V}{dkT}\right). \tag{1}$$

Thus, the particles become "looser," which facilitates, in particular, the course of such processes as diffusion and dissolution of atoms in the particles. The rate of chemical reaction in particles can also depend on their size, since the frequency of collisions of atoms (molecules) of reacting components in the particles will depend on their diffusion coefficients, which in turn depend on the concentration of vacancies in the particles.

The influence of the size of a particle on the course of a chemical reaction in it will be considered by the example of oxidation of a silicon nanoparticle. Here we will use the model proposed in [4] that assumes that the chemical reaction of molecular oxygen with silicon proceeds over the entire volume of the substance, and the reaction product is silicon dioxide:

$$\text{Si} + \text{O}_2 = \text{SiO}_2\,. \tag{2}$$

Next we will consider the stage of the process, where the number concentrations of oxygen molecules in the particle c_1 and the reaction product (silicon dioxide) can be assumed to be substantially below the number concentrations of silicon atoms c_2, so that the value of c_2 can be approximated as constant. For simplicity we will not consider the situation where oxygen molecules diffuse through the silicon dioxide layer formed at the gas-condensed interface. With regard to the assumptions made, for the distribution of the number concentration of oxygen molecules in a spherical silicon particles we have the equation

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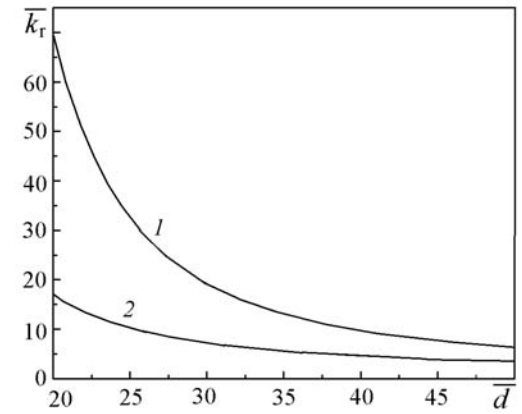

Fig. 1. Dependence of the dimensionless rate constant of chemical reaction of oxidation of silicon nanoparticle $\overline{k}_r$ on the dimensionless nanoparticle diameter $\overline{d}$ at E_∞ = 2.53 eV: 1) T = 1200 K; 2) 1800.

$$\frac{\partial c_1}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c_1}{\partial r}\right) - k_r c_1 c_2 , \tag{3}$$

where

$$D = D_0 \exp\left(-\frac{E}{kT}\right). \tag{4}$$

Here E is the activation energy of oxygen diffusion in silicon; in a massive sample this energy can be estimated as 2.53 eV [4], and the pre-exponential factor D_0 is assumed constant and equal to 0.13 cm^2/sec [4].

Following [4], we present the reaction rate constant k_r as

$$k_r = 4\pi R_0 D , \tag{5}$$

where R_0 is the radius of interaction of an oxygen molecule with a silicon atom; next R_0 is considered constant (note that generally in (5) the diffusion coefficient can be modified with regard to the mobility of both components [5]; however, for simplicity we will use, according to [4], expression (5) to evaluate the quantity k_r).

By analogy with [1], we assume that the following relation between the activation energies of the diffusion of oxygen molecules in a nanosized silicon particle (E_p) and in a massive silicon sample (E_∞) is fulfilled:

$$\frac{E_p}{E_\infty} = \frac{T_{m,p}}{T_{m\infty}} , \tag{6}$$

where $T_{m,p}$ and $T_{m\infty}$ are the melting temperatures for the silicon nanoparticle and massive sample, respectively.

Following [6], the dependence of the melting temperature on the particle diameter can be written as

$$T_{m,p} = T_{m\infty} \exp\left(-\frac{4\delta}{\delta + d}\right), \tag{7}$$

where δ is the so-called Tolman length which, according to [7], changes depending on the substance within the limits 0.096–0.35 nm. Subject to Eqs. (5)–(7), the following expression for the reaction rate constant k_r can be written:

$$k_r = 4\pi R_0 D_0 \exp\left[-\frac{E_\infty}{kT}\exp\left(-\frac{4}{1+\overline{d}}\right)\right], \tag{8}$$

where $\overline{d} = d/\delta$.

Figure 1 gives the dependence of the dimensionless value of $\overline{k}_r = k_{r,p}/k_{r\infty}$, where $k_{r\infty}$ is the reaction rate constant for a massive sample ($d \to \infty$). It is seen that $\overline{k}_r$ increases with a decrease in the particle size.

Problems on the course on a chemical reaction in a nanoparticle can be arbitrarily divided into two types. The first type includes the situation where at the initial instant of time oxygen begins to arrive at a nanoparticle and react with silicon atoms there. The second type comprises the problems in which the concentration of oxygen in the particle decreases with time due to its reaction with silicon. In the case of the problems of the first type, it is necessary to solve Eq. (3) under the following initial and boundary conditions (in what follows the surface coverage by oxygen molecules is assumed to be significantly smaller than unity):

$$c_1 \big|_{t=0} = 0\,, \tag{9}$$

$$D \frac{\partial c_1}{\partial r}\bigg|_{r=0} = 0\,, \tag{10}$$

$$D \frac{\partial c_1}{\partial r}\bigg|_{r=r_0} = k_{\mathrm{ad,ab}} n_1 - k_{\mathrm{ab,ad}} c_1 (r_0)\,, \tag{11}$$

where n_1 is determined as

$$\frac{dn_1}{dt} = \alpha J + k_{\mathrm{ab,ad}} c_1 (r_0) - \frac{n_1}{\tau} - k_{\mathrm{ad,ab}} n_1 - J_{\mathrm{s}}\,, \tag{12}$$

$$n_1 \big|_{t=0} = 0\,. \tag{13}$$

The first two terms on the right-hand side of Eq. (12) describe the arrival of oxygen molecules at the adsorption position on the nanoparticle, which is related to their adsorption on incidence from the gas phase and transition from the absorption position into the adsorption one. The third, fourth, and fifth terms describe a loss of adsorbed oxygen molecules in the adsorption layer as a result of desorption, transition of oxygen molecules into the absorption position, as well as due to the chemical reaction between the adsorbed oxygen molecules and surface silicon atoms. On the assumption that the chemical reaction on the nanoparticle surface is realized through interaction of the adsorbed oxygen molecules and silicon atoms, we can write the expression for the rate of chemical reaction on the surface J_{s}:

$$J_{\mathrm{s}} = k_{\mathrm{r,s}} n_1 n_2\,. \tag{14}$$

We assume that, similarly to the above relation between the concentrations of components in the bulk phase, the number concentrations of oxygen molecules n_1 and reaction product (silicon dioxide) in the surface (adsorbed) layer are substantially below the number concentration of silicon atoms in the surface layer, and the value of n_2 can be approximately considered constant.

In a free-molecular regime of gas flow, when the mean free path of molecules greatly exceeds the particle size, the quantity J in (12) on the assumption of the Maxwellian distribution function for the molecules incident on the particle looks like

$$J = \frac{n_{1\mathrm{g}} v_{1\mathrm{g}}}{4}\,. \tag{15}$$

In the flow regime mentioned, the number concentration of oxygen molecules $n_{1\mathrm{g}}$ near the particle surface can be considered equal to its value in the gas phase far away from the particle. Here, the size effects will manifest themselves through the parameters α, τ, $k_{\mathrm{ad,ab}}$, $k_{\mathrm{ab,ad}}$, k_{r}, $k_{\mathrm{r,s}}$, and D. It should be noted that by now the dependence of the given parameters on the size of particles has not been adequately investigated. For some of them, the noted dependence is of opposite character. For example, as indicated earlier, the quantity k_r can increase with decreasing particle diameter. However, the value of the sticking coefficient α can decrease with decreasing particle size [8, 9]. The value of τ can also decrease with particle size due to decrease in the adsorption energy. The circumstances mentioned complicate an analysis of the formulated problem, which is connected with the processes occurring at the interface. Moreover, in the case where a gas flow regime cannot be considered as free-molecular, the value of J should be found either from the solution of the kinetic equation for the velocity distribution function for oxygen molecules in the gas phase (which gives the most exact value of J) or from an approximate approach based on the following diffusion equation for the quantity n_{1g} [10]:

$$\frac{\partial n_{1g}}{\partial t} = \frac{D_g}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial n_{1g}}{\partial r} \right) \quad \text{at} \quad r > r_0 , \tag{16}$$

with regard to the initial and boundary conditions

$$n_{1g}(r, t) = n'_{1g} \quad \text{at} \quad r > r_0 , \quad t = 0 ; \tag{17}$$

$$n_{1g}(r, t) = n'_{1g} \quad \text{at} \quad r \to \infty , \quad t > 0 ; \tag{18}$$

$$D_g \left. \frac{\partial n_{1g}}{\partial r} \right|_{r=r_0} = \frac{\alpha n_{1g}(r_0)\, v_{1g}}{4} - \frac{n_1}{\tau} . \tag{19}$$

The value of the density of the resulting flux of oxygen molecules entering into the particle will generally depend on the diffusion coefficient of these molecules in the gas phase and on the particle size, which leads to the dependence of the mentioned flux density on the Knudsen number defined by the ratio of the mean free path of the molecules to the particle radius. Subject to Eqs. (3)–(19), under the assumptions made, the value of $c_1(r, t)$ can be found, which makes it possible to describe the process of silicon particle oxidation on oxygen supply into the particle from the gas phase. It should be noted that generally a situation can be realized where a layer of the reaction product (silicon dioxide) is formed on the gas-condensed phase interface; in this case oxygen molecules will diffuse through the layer mentioned and then react with silicon atoms.

We consider the problem of the second type, where oxygen initially is present in the particle and its concentration there decreases with time as a result of the chemical reaction between oxygen molecules and silicon atoms. In the case where the emergence of oxygen molecules from the particle and their entry into the particle from the gas phase can be neglected, there is no need to analyze the processes proceeding in the gas phase and at the interface to estimate the influence of the size effect upon a decrease in the oxygen concentration in the nanoparticle. For simplicity, next we assume a uniform oxygen distribution over the particle volume and a constant number concentration of silicon atoms, which is equal to its value at $t = 0$ ($c_2 = c_{20}$). In the case considered, the dependence of the relative concentration of oxygen molecules on time $\bar{c}_1(t) = c_1(t)/c_1$ ($t = 0$), subject to (3) and the assumptions made, can be written as

$$\bar{c}_1 = \exp\left\{ -4\pi R_0 D_0 c_{20} t \exp\left(-\frac{E_\infty}{kT} \exp\left(-\frac{4}{1+\bar{d}} \right) \right) \right\} . \tag{20}$$

It follows from formula (20) that a decrease in the oxygen concentration to a certain value in a small nanosized particle occurs in a shorter time as compared to a massive sample.

We note that an increase in mobility of atoms (molecules) in nanoparticles in comparison with a massive sample can lead to a higher nucleation rate of the substance in the nanoparticle, which represents a supersaturated solution. It is known that the nucleation rate increases with the flux density of atoms into the particle (cluster) being formed. In turn, the flux density of atoms into the cluster increases with the diffusion coefficient of atoms in a condensed phase. In the case where nucleation occurs in nanoparticles, a decrease in the activation energy for diffusion process of atoms in nanoparticles with a decrease in their size will lead to an increase in the nucleation rate.

Thus, by the example of the chemical reaction of oxidation of a nanosized silicon particle, we have demonstrated that the chemical reaction in the particle can occur with a higher rate than in a massive sample due to the higher mobility of reacting molecules. Cases have been considered where oxygen arrives at the particle from the outside gas phase and reacts with silicon atoms inside the particle, as well as where oxygen is initially present in the nanoparticle and its concentration there decreases with time as a result of the chemical reaction. It has been shown that in the first case the influence of the size effects on the course of chemical reaction can be accompanied by an opposite dependence of some parameters on the particle size. It has been noted that the nucleation process in a nanosized particle can occur with a higher rate than in a massive sample.

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NOTATION

c, concentration; D, diffusion coefficient of oxygen molecules in silicon; D_g, diffusion coefficient of oxygen molecules in a gas phase; d, particle diameter; J, flux density of oxygen molecules incident on the particle surface; k, Boltzmann constant; k_r, rate constant of chemical reaction in the particle; $k_{ad,ab}$ and $k_{ab,ad}$, rate constants of transition of an oxygen molecule respectively from adsorption position to absorption one and back; $k_{r,s}$, rate constant of reaction of oxygen molecules with silicon atoms in a surface layer; n_1, number density of adsorbed oxygen molecules; n_2, number density of silicon atoms in the surface layer with which oxygen molecules react; n_{1g}, number density of oxygen molecules in a gas phase; r, radial coordinate reckoned from the particle center; r_0, particle radius; T, temperature; t, time; V, volume per atom; v_{1g}, mean velocity of oxygen molecules in a gas phase; α, sticking coefficient of oxygen molecules; σ, specific surface energy; τ, adsorption time of oxygen molecules on the surface of the silicon nanoparticle. Subscripts: ad, adsorption; ab, absorption; g, gas phase; m, melting; p, particle; r, reaction; s, surface layer; 1, oxygen; 2, silicon; ∞, bulk phase.

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