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USE OF THE LENNARD-JONES POTENTIAL IN MODELING THE ABSORPTION DEFORMATION OF MICROPOROUS CARBON ADSORBENTS

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A molecular-statistical model for description of the elastic absorption deformation of microporous carbon adsorbents in interaction with gases has been proposed. The results of modeling for the CO_2–AUK microporous carbon absorbent system have been compared to experimental data.

Introduction. The method in which the role of the adsorbent surface is reduced only to the creation of an adsorption field is widely used at present for description of adsorption equilibrium. The assumption that the adsorbent is absolutely inert makes it possible to substantially simplify the description of the equilibrium, but it is inadequate from the physical viewpoint.

Consideration of the adsorbent as being inert, even in the simplest case — that of adsorption on a plane homogeneous surface — requires that the adsorbent deformation be additionally allowed for in calculations. One reason for the deformation is the decrease in the uncompensated forces applied to the surface of the adsorbent atoms due to their interaction with the adsorbate molecules. The value of the adsorption deformation is dependent on the properties of an adsorption system; however, even small deformations are capable of exerting a substantial influence on the system's thermodynamic characteristics determined experimentally [1].

Among the works devoted to investigation and description of adsorption deformation, we can single out those on deformation of clay materials [2, 3], polymers [4, 5], and microporous carbon adsorbents [6, 7]. The model proposed is intended for description of the elastic adsorption deformation of microporous carbon adsorbents in interaction with gases using the Lennard-Jones potential.

Description of the Model. Assuming that microporous carbon adsorbents have a homogeneous microporous structure, we consider the adsorbent in the first approximation in the form of a parallelepiped with uniformly distributed cylindrical micropores of equal diameter. A diagrammatic representation of the adsorbent is given in Fig. 1.

The initial volume of the specimen modeled is $V_0 = xyz$, and the volume under the conditions of free expansion (compression) is

$$V = x\left(1 + \frac{\Delta x}{x}\right) y \left(1 + \frac{\Delta y}{y}\right) z \left(1 + \frac{\Delta z}{z}\right).$$

Assuming that the adsorbent deformation is isotropic, i.e.,

$$V = V_0 \left(1 + \frac{\Delta l}{l}\right)^3 ,$$

where $\Delta l/l = \Delta x/x = \Delta y/y = \Delta z/z$, we obtain an expression relating the change in its volume to the relative linear deformation:

$$\Delta V = V_0 \left[\left(1 + \frac{\Delta l}{l}\right)^3 - 1\right]. \quad (1)$$

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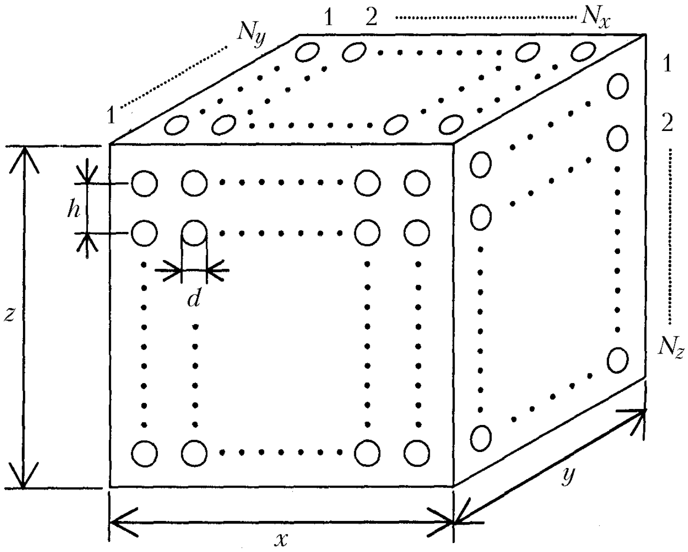

Fig. 1. Structural model of the adsorbent specimen.

The initial volume of micropores is

$$V_{\mathrm{p},0} = \frac{\pi d^2}{4} k_{\mathrm{cr}} \left(N_x N_y z + N_x N_z y + N_y N_z x\right)$$

or, taking into account that $N_x = x/h$, $N_y = y/h$, and $N_z = z/h$, we can represent it in the form

$$V_{\mathrm{p},0} = k_{\mathrm{p},0} V_0 ,$$

where $k_{\mathrm{p},0} = \dfrac{3\pi d^2 k_{\mathrm{cr}}}{4h^2}$ is the initial porosity of the adsorbent.

The volume of micropores in isotropic deformation is calculated as follows:

$$V_{\mathrm{p}} = \frac{\pi d^2 \left(1 + \frac{\Delta d}{d}\right)^2}{4} k_{\mathrm{cr}} \left(N_x N_y z \left(1 + \frac{\Delta l}{l}\right) + N_x N_z y \left(1 + \frac{\Delta l}{l}\right) + N_y N_z x \left(1 + \frac{\Delta l}{l}\right)\right)$$

or

$$V_{\mathrm{p}} = V_0 k_{\mathrm{p},0} \left(1 + \frac{\Delta d}{d}\right)^2 \left(1 + \frac{\Delta l}{l}\right).$$

Accordingly, the change in the micropore volume is found as

$$\Delta V_{\mathrm{p}} = V_0 k_{\mathrm{p},0} \left[\left(1 + \frac{\Delta l}{l}\right)\left(1 + \frac{\Delta d}{d}\right)^2 - 1\right]. \tag{2}$$

If the density of the adsorbent solid phase is constant, the equality of the right-hand sides of expressions (1) and (2)

$$\left(1 + \frac{\Delta l}{l}\right)^3 - 1 = k_{\mathrm{p},0} \left[\left(1 + \frac{\Delta l}{l}\right)\left(1 + \frac{\Delta d}{d}\right)^2 - 1\right]$$

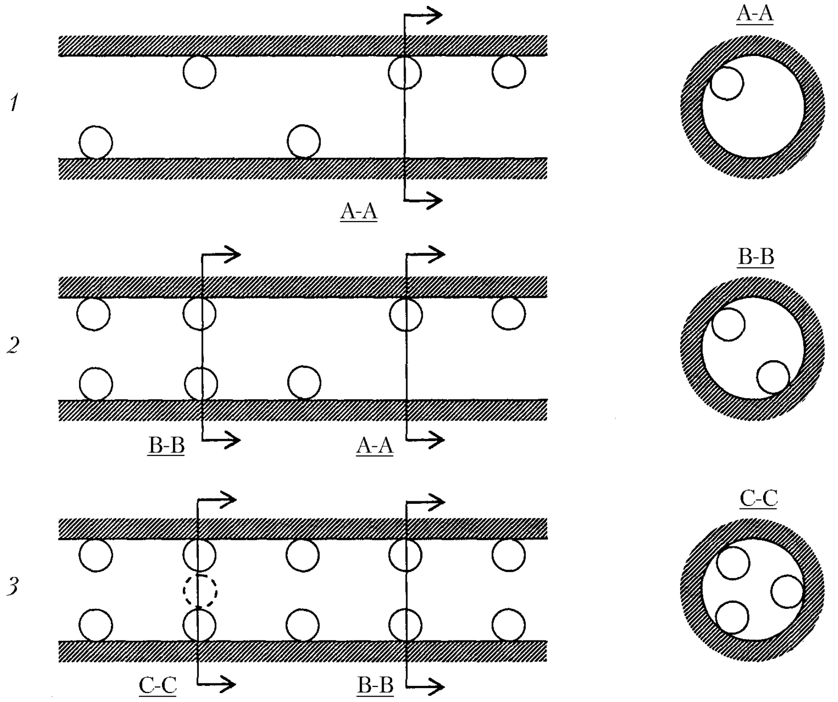

Fig. 2. Modeled filling of the adsorbent micropore: 1) one molecule; 2) two molecules; 3) three molecules.

is true. According to [6, 7], the relative deformation is small; therefore, the approximate equality

$$\frac{3\Delta l}{l} \approx k_{\mathrm{p},0}\left[\left(1+\frac{\Delta l}{l}\right)\left(1+\frac{2\Delta d}{d}\right)-1\right]$$

or

$$\frac{\Delta l}{l} \approx \frac{2k_{\mathrm{p},0}\,(\Delta d/d)}{3-k_{\mathrm{p},0}\,(1+(\Delta d/d))} \tag{3}$$

also holds. Thus, it can be stated that the relative linear deformation of the specimen modeled is quasilinearly related to the relative change in the diameter of its micropores.

For convenience of the description of the process of adsorption in micropores in modeling we break them into fragments whose length corresponds to the average geometric dimensions of the adsorbate molecules. We consider successive filling of all the fragments first with one absorbate molecule, next with two molecules, etc. (Fig. 2).

The adsorbent micropores in the course of the adsorption are generally deformed under the action of both the external forces applied to the adsorbent and the internal ones. However, according to [6, 7], in considering microporous carbon adsorbents, we can restrict ourselves to allowance just for the internal forces playing a leading role in adsorption deformations.

The internal forces causing the deformation of a micropore are related to the interaction of the adsorbate molecules with the surface atoms (F_1), the mutual interaction of the adsorbate molecules (F_2), and also to the impacts of the molecules of an adsorbed gas with the micropore walls due to their thermal motion (F_3):

$$F = F_1 + F_2 + F_3\,. \tag{4}$$

The interaction of the adsorbed molecules with the surface adsorbent atoms is the most difficult to describe. However this interaction can be described classically in the language of model potential functions as the interaction of molecules with solid surfaces in a fairly wide range of variation of the parameters of the adsorption system [8]. The solid surfaces are considered in this case as a set of atoms and the potential of interaction of the adsorbate molecules with the surface is sought in the form of the sum of the potentials of interaction of the molecules with all the surface atoms:

$$U_{\mathrm{m-a}}\left(|\mathbf{r}|\right)=\sum_{i=1}^{N_{\mathrm{m}}}\sum_{j=1}^{N_{\mathrm{a}}} u_{\mathrm{m}(i)-\mathrm{a}(j)}\left(\left|\mathbf{r}_{\mathrm{m}(i)}-\mathbf{r}_{\mathrm{a}(j)}\right|\right). \tag{5}$$

Such an approach has also been realized in the model proposed; the sum of the potentials of interaction with all the surface atoms has been replaced by the sum of the potentials of interaction with active sites, by which we mean the portions of the pore surface on which the gas molecules can be adsorbed (or have already been adsorbed). The number of active sites is determined by the maximum possible number of gas molecules adsorbed in the micropore.

The potential of one adsorbed molecule can be found as follows:

$$U_{\mathrm{m}}\left(|\mathbf{r}|\right)=\sum_{i=1}^{N_{\mathrm{a.s-1}}} u_{\mathrm{m-a.s}(i)}\left(\left|\mathbf{r}_{\mathrm{m}}-\mathbf{r}_{\mathrm{a.s}(i)}\right|\right)+u^{*}_{\mathrm{m-a.s}(0)}\left(\left|\mathbf{r}_{\mathrm{m}}-\mathbf{r}_{\mathrm{a.s}(0)}\right|\right), \tag{6}$$

where $u^{*}_{\mathrm{m-a.s}(0)}$ refers to the active site with which the molecule interacts directly.

As the equation of couple-interaction potential, we have selected the Lennard-Jones potential as that most frequently used in numerical modeling (the parameters of the potential are determined by the properties of the system in question):

$$u\left(r\right)=4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12}-\left(\frac{\sigma_{ij}}{r}\right)^{6}\right]. \tag{7}$$

Assuming that the interactions in question are realized in the potential field of forces, we can pass from the potential (6) to the sought interaction force $f = -\partial u/\partial r$:

$$f\left(r\right)=4\varepsilon_{ij}\left[\frac{12\sigma_{ij}^{12}}{r^{13}}-\frac{6\sigma_{ij}^{6}}{r^{7}}\right]. \tag{8}$$

Then the resultant force vector acting on the pore surface upon the arrival of one adsorbed molecule can be found as

$$\mathbf{f}_1\left(|\mathbf{r}|\right)=\sum_{i=1}^{N_{\mathrm{a.s-1}}} f_{\mathrm{m-a.s}(i)}\left(\left|\mathbf{r}_{\mathrm{m}}-\mathbf{r}_{\mathrm{a.s}(i)}\right|\right)\mathbf{r}^{1}_{\mathrm{m-a.s}(i)}+f^{*}_{\mathrm{m-a.s}(0)}\left(\left|\mathbf{r}_{\mathrm{m}}-\mathbf{r}_{\mathrm{a.s}(0)}\right|\right)\mathbf{r}^{1}_{\mathrm{m-a.s}(0)}, \tag{9}$$

where $\mathbf{r}^{1}_{\mathrm{m-a.s}(i)} = (\mathbf{r}_{\mathrm{m}} - \mathbf{r}_{\mathrm{a.s}(i)})/\left|\mathbf{r}_{\mathrm{m}}-\mathbf{r}_{\mathrm{a.s}(i)}\right|$ and $\mathbf{r}^{1}_{\mathrm{m-a.s}(0)} = (\mathbf{r}_{\mathrm{m}} - \mathbf{r}_{\mathrm{a.s}(0)})/\left|\mathbf{r}_{\mathrm{m}}-\mathbf{r}_{\mathrm{a.s}(0)}\right|$ are the unit vectors of the direction of interaction.

The mutual interaction of the adsorbate molecules can also be described using the Lennard-Jones potential (7) by determining the interaction force sought from expression (8):

$$\mathbf{f}_2\left(|\mathbf{r}|\right)=\sum_{i=1}^{N_{\mathrm{m}}-1} f_{\mathrm{m-m}(i)}\left(\left|\mathbf{r}_{\mathrm{m}}-\mathbf{r}_{\mathrm{m}(i)}\right|\right)\mathbf{r}^{1}_{\mathrm{m-m}(i)}; \tag{10}$$

here $\mathbf{r}^{1}_{\mathrm{m-m}(i)} = (\mathbf{r}_{\mathrm{m}} - \mathbf{r}_{\mathrm{m}(i)})/\left|\mathbf{r}_{\mathrm{m}}-\mathbf{r}_{\mathrm{m}(i)}\right|$. The interaction parameters ε_{ij} and σ_{ij} are tabulated for most gases and are presented, for example, in [9].

The value of the force F_3 characterizing deformation from the impacts of gas molecules due to their thermal motion is generally determined by the concentration of colliding molecules per unit volume and by their kinetic en-

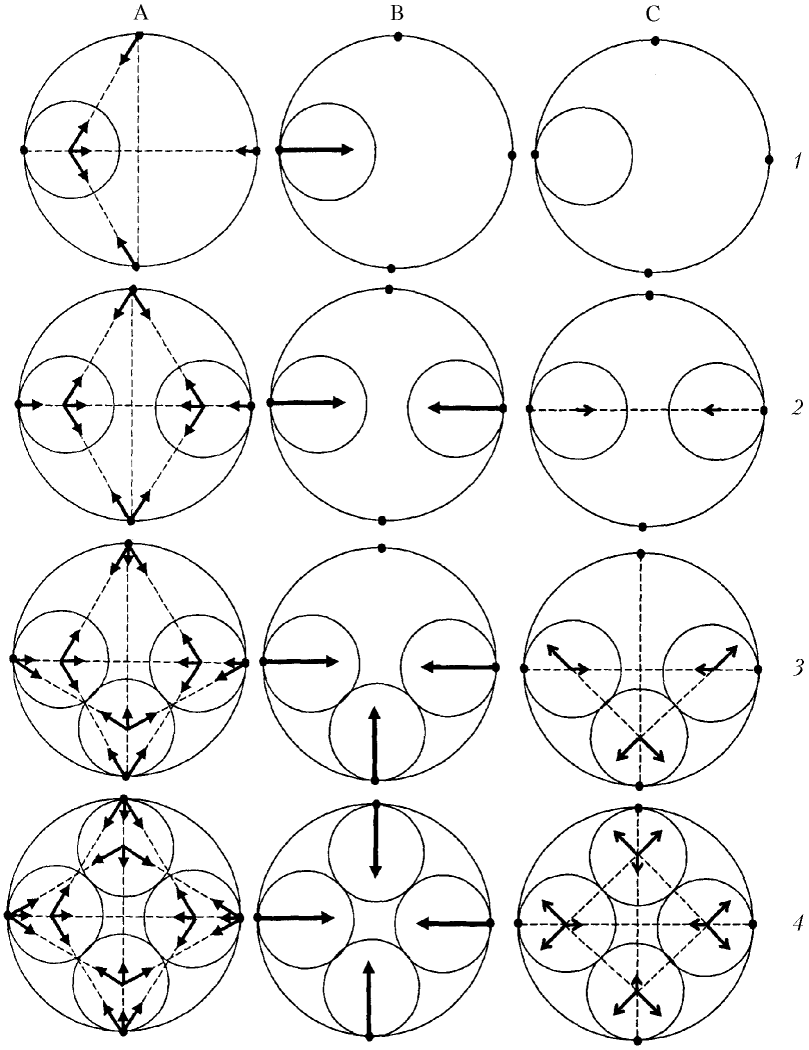

Fig. 3. Deforming forces acting in the micropore cross section: 1) in adsorption of one molecule; 2) of two molecules; 3) of three molecules; 4) of four molecules; A) forces of interaction with active sites; B) resultant force of interaction with the active site with which the molecule interacts directly; C) forces of interaction between adsorbate molecules.

ergy. In considering the adsorption deformation in the region of low temperatures, we can disregard the force F_3 in the first approximation.

Assuming that the deformation of a micropore is caused by the forces acting along the normal to its surface, we can also disregard, in the first approximation, the interaction of adsorbate molecules with each other and with active centers in different fragments (they are small in value or have a predominant direction along the micropore axis). Thus, to evaluate the internal forces it is sufficient to calculate and sum up the forces acting on the micropore surface in one fragment.

The dependence which is true for the elastic deformation

$$\frac{\Delta d}{d} = k_{\mathrm{d}} F, \tag{11}$$

makes it possible to relate the found value of the total force to the sought value of the linear deformation $\Delta l/l$ using (3).

We can single out the following assumptions of the model proposed:

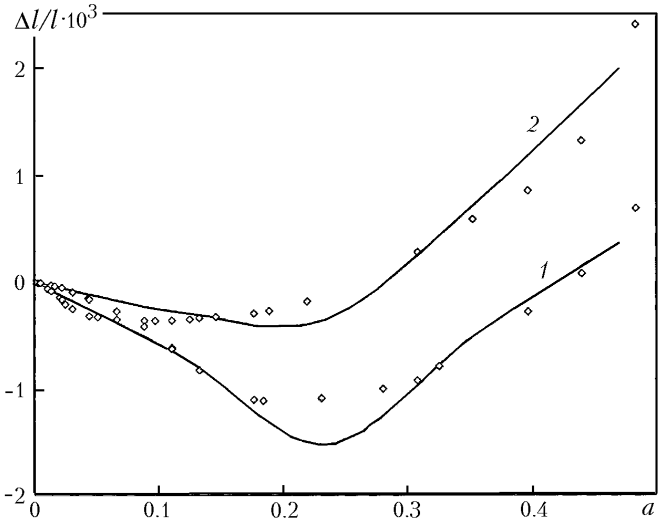

Fig. 4. Comparison of the results of modeling (solid curves) and the experimental isotherms (points) of relative deformation of an AUK microporous carbon adsorbent in adsorption of carbon dioxide: 1) $T = 243$; 2) 273 K.

(1) idealization of the adsorbent structure and the filling of micropores in the course of the adsorption;

(2) use of the semiempirical Lennard-Jones potential for determination of the interaction force;

(3) neglect of the deformation caused by the impacts of adsorbed molecules with the micropore walls due to their thermal motion;

(4) the internal forces causing the deformation are potential, whereas the deformation itself is elastic.

Modeling. A comparison of calculated and experimental data is an important criterion of applicability of any theoretical considerations. For this purpose, the experimental data, i.e., the isotherms of adsorption deformations of an AUK microporous carbon adsorbent in interaction with CO_2, published in [6] were compared to the data obtained during the modeling.

In calculations with allowance for the characteristics (given in [6]) of the AUK microporous carbon adsorbent, the initial diameter of the micropores was taken to be $d = 9.1$ Å. The shape of the CO_2 molecules was assumed to be spherical with a sphere radius of 1.88 Å. The parameters of the potential of interaction of the adsorbate molecules with the micropore surface were determined from the isosteric adsorption heats in the region of small fillings and with allowance for the geometric dimensions of the adsorbate molecules: $\varepsilon_{\text{m–a.s}}/k = 2566$ K and $\sigma_{\text{m–a.s}} = 1.67$ Å. The parameters of the potential of interaction of the carbon dioxide molecules were $\varepsilon_{\text{m–m}}/k = 100.2$ K and $\sigma_{\text{m–m}} = 3.76$ Å, according to [9].

Geometric interpretation of forces acting in modeling the deformation in the micropore cross section is presented in Fig. 3 (the forces acting in the cross-sectional plane are indicated). To partially allow for the nonpotential character of interactions and the thermal motion of molecules we numerically prescribed, in the calculations, the force of indirect action on the micropore wall from the molecule adsorbed.

We restricted ourselves to a detailed consideration just of one cross section in modeling.

The value of the resultant force acting on the interior surface can be assumed to be virtually linearly related to the deformation characteristic sought, according to expressions (3) and (11). Therefore, the coefficient of proportionality between the force found and the relative linear deformation was determined by comparing to the data obtained experimentally.

Figure 4 gives the results of modeling and the experimental deformation curves for temperatures of 243 and 273 K. Despite the fact that the model has certain constraints noted above, the modeling results obtained for the above temperatures are quite satisfactory. For modeling of adsorption deformation at higher temperatures, we must additionally allow for the thermal motion of molecules in the calculations.

Conclusions. The model proposed describing the elastic adsorption deformation of microporous carbon adsorbents in interaction with gases makes it possible to relate the micro- and macroparameters of the adsorbent–adsorbate system in question. The possibility of applying it to evaluation of the adsorption deformation is confirmed by the satisfactory coincidence of the results of the calculations carried out for the CO_2–AUK microporous carbon adsorbent system with experimental data.

NOTATION

a, running value of the equilibrium adsorption, kg/kg; d, initial diameter of micropores, m; F, resultant force causing deformation, N; f, interaction force, N; $f_{\mathrm{m-a.s}(i)}$, force of interaction of an adsorbate molecule with the ith active site, N; $f^*_{\mathrm{m-a.s(0)}}$, force of interaction of an adsorbate molecule with the active site with which the molecule interacts directly, N; $f_{\mathrm{m-m}(i)}$, force of interaction of an adsorbate molecule with the ith adsorbed molecule, N; h, initial distance between the centers of micropores, m; k, Boltzmann constant, J/K; k_{d}, coefficient of proportionality between the force and the relative deformation of the micropore diameter, 1/N; k_{cr}, coefficient allowing for the crookedness of micropores; N_{a}, number of surface atoms; $N_{\mathrm{a.s}}$, number of active sites; N_{m}, running number of adsorbed molecules; N_x, N_y, and N_z, number of micropores in the specimen modeled; T, temperature, K; $U_{\mathrm{m-a}}$, potential of interaction of adsorbed molecules with the adsorbent surface, J; U_{m}, potential of interaction of one adsorbate molecule with the micropore surface, J; u, interaction potential, J; $u_{\mathrm{m}(i)-\mathrm{a}(j)}$, potential of pair interaction of an adsorbate molecule with the ith active site, J; V and V_0, running and initial volume of the adsorbent, m^3; V_{p} and $V_{\mathrm{p},0}$, running and initial volume of the adsorbent micropores, m^3; r, distance, m; $\mathbf{r}$, radius vector, m; $\mathbf{r}_{\mathrm{a}(j)}$, radius vector of the jth surface atom, m; $\mathbf{r}_{\mathrm{a.s(0)}}$, radius vector of the active site with which the molecule interacts directly, m; $\mathbf{r}_{\mathrm{a.s}(i)}$, radius vector of the ith active site, m; $\mathbf{r}_{\mathrm{m}}$, radius vector of the adsorbate molecule in question, m; $\mathbf{r}_{\mathrm{m}(i)}$, radius vector of the ith adsorbate molecule; x, y, and z, dimensions of the undeformed adsorbent, m; $\Delta d/d$, relative change in the diameter of the adsorbent micropores; $\Delta l/l$, relative linear deformation of the adsorbent; $\Delta x/x$, $\Delta y/y$, and $\Delta z/z$, relative linear deformations of the adsorbent along the axes; ΔV, change in the volume of the adsorbent under deformation, m^3; ΔV_{p}, change in the volume of the adsorbent micropores under deformation, m^3; ε_{ij}, potential-well depth, J; $\varepsilon_{\mathrm{m-a.s}}$, potential-well depth in interaction of an active site and an adsorbate molecule, J; $\varepsilon_{\mathrm{m-m}}$, potential-well depth in interaction of adsorbate molecules, J; $\sigma_{ij}/2$, effective repulsion radius, m; $\sigma_{\mathrm{m-a.s}}/2$, effective repulsion radius in interaction of an active site and an adsorbate molecule, m; $\sigma_{\mathrm{m-m}}/2$, effective repulsion radius in interaction of adsorbate molecules, m. Subscripts: 0, initial value; a, atom; a.s, active site; d, deformation; m, (adsorbed) molecule; p, pore; cr, crookedness.

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