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AFM application for *in situ* study of the adsorptions processes

© E.A. Sosnov, S.A. Belova, A.A. Malygin

St. Petersburg State Technological Institute,
198013 St. Petersburg, Russia

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The comparison of calculated and experimental data allows to assume the following mechanism of H_2O adsorption in dynamic conditions at high temperature: during the adsorption of the first portions of sorbate on the silica gel surface the thin film of water overlappes the access to an intrapore space and the adsorption proceeds only on an exterior surface of a sorbent.

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1. Introduction

The invention of scanning tunnelling (1981), and later atomic force microscopy (AFM) (1986) — the methods with high sensitivity and resolution, has made possible the direct examinations of topography and the physicochemical properties of a surface of solids. The modern evolutions of scanning probe microscopy methodology allow expanding the sphere of examinations, including carrying out the direct study of physical processes leakage at the surface of solids. This work is devoted to the investigation by AFM methods in situ of water vapour adsorption on the wide-porous silica gels in dynamic regimes.

The silica gel ShSKG and indicator vanadium-containing silica gel IVS-1 received by processing of ShSKG by $VOCl_3$ vapours by the molecular layering method [1,2] were studied. As is known, IVS-1 shows the indicator properties in relation to H_2O vapours (colour transition in the adsorbate quantities interval $a_{H_2O} = 0-12$ mmol/g: white–yellow–orange–red–claret with wide gamma of the intermediate colour nuances [3]). It allows to estimate the quantity of adsorbed waters by silica gel metachromatism. The specified property of indicator silica gel in spite of the fact that water vapour adsorption velocity of IVS-1 surpasses the analogous parameter fo ShSKG [4], has been used for an estimation of adsorbate quantity of ShSKG silica gel, yielding a little overstimated value.

2. Experimantal part

The examinations were carried out on scanning probe microscope (SPM) Solver P47 Pro[1] (JSC NT-MDT, Russia). Measuments were taken by AFM methods with using of NSG-01 cantilever at a water adsorption from air on the surface of silica gel spherical particles (⌀ 2.5–3.0 mm). For decreasing of water vapour adsorption velocity the recycled at 400°C within 2 h [4] sorbent was placed on preheated SPM objective table where the matrix temperature $130 \pm 2^\circ$C was supported.

3. Results and discussion

The topography of initial silica gel ShSKG before water vapour adsorption are presented at Fig. 1, *a*. The analysis of topography has shown that the homogeneous globular structure with a medial size of globule 180–200 nm is observed at the silica gel surface. At the same time the calculation of structural characteristics of a silica gel (see Table) allows to estimate that a size of one globule is ~ 10 nm. This calculation has been carried out on a procedure [5] on the basis of experimental data for specific surface area (S_{SURF}) and volume of pore (V_{P}). Because the structures of disperse silica are close to various facets of β-crystabalit [6,7], the density of silica gel for calculations was accepted equal density of β-crystabalit (2.32 g/cm^3 [8]).

Considering the splicing of separate globules among themselves (the calculated number of contacts of a separate globule with next is 3.95) and the size of structures observed on Fig. 1, *a*, it is possible to assume, that on the silica gel surface has been observed not separate globules (which size is comparable to resolving properties of SPM), and they are joint to larger formations.

AFM-investigation of IVS-1 (Fig. 1, *b*, *c*) has shown, that at the increasing of the quantity of adsorbed water, which fixed by changing of sorbent colour [3], the appreciable increasing of agglomerates of silica globules size (up to 3.0 microns at H_2O adsorption of 4.0 mmol/g (Fig. 1, *c*)) was observed. During the increasing of quantity of adsorbed water the increment of surface structures sizes and washout of their boundary lines is observed.

The local force spectroscopy [9] was carried out on the surface of explored sorbents during the dynamic adsorption of water vapor. The results are given on Fig. 2. It is known, that the studying of curves of AFM probe interacting with a surface in presentation „force–distance“ allows to define the differences in chemical structure and properties of separate areas of surface of solid. Discussing the model curve (Fig. 3), it is necessary to note that if the material surface is liquid, a hysteresis is observed between the curves ABC and CBDEA corresponding to the input and output of the AFM probe into the liquid surface. The size of this hysteresis matches to the thickness of liquid layer.

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[1] The investigations were carried out at the TsKP „Chemical Assembling of Nanomaterials“, St. Petersburg, State Technological Institute (Technical University), Russia

From the analysis of the results presented on Fig. 2, it is established, that after the silica gels contact with water vapour at 130°C in a dynamic regime during 10–15 min ($a_{H_2O} \approx 1.5$ mmol/g) the thickness of adsorbed water film is 13–15 and 19–20 nm for ShSKG and IVS-1 accordingly. After the increasing of a contact time up to 50 min ($a_{H_2O} \approx 4.0$ mmol/g) the thickness of water on the surface increases up to 30 and 40 nm accordingly.

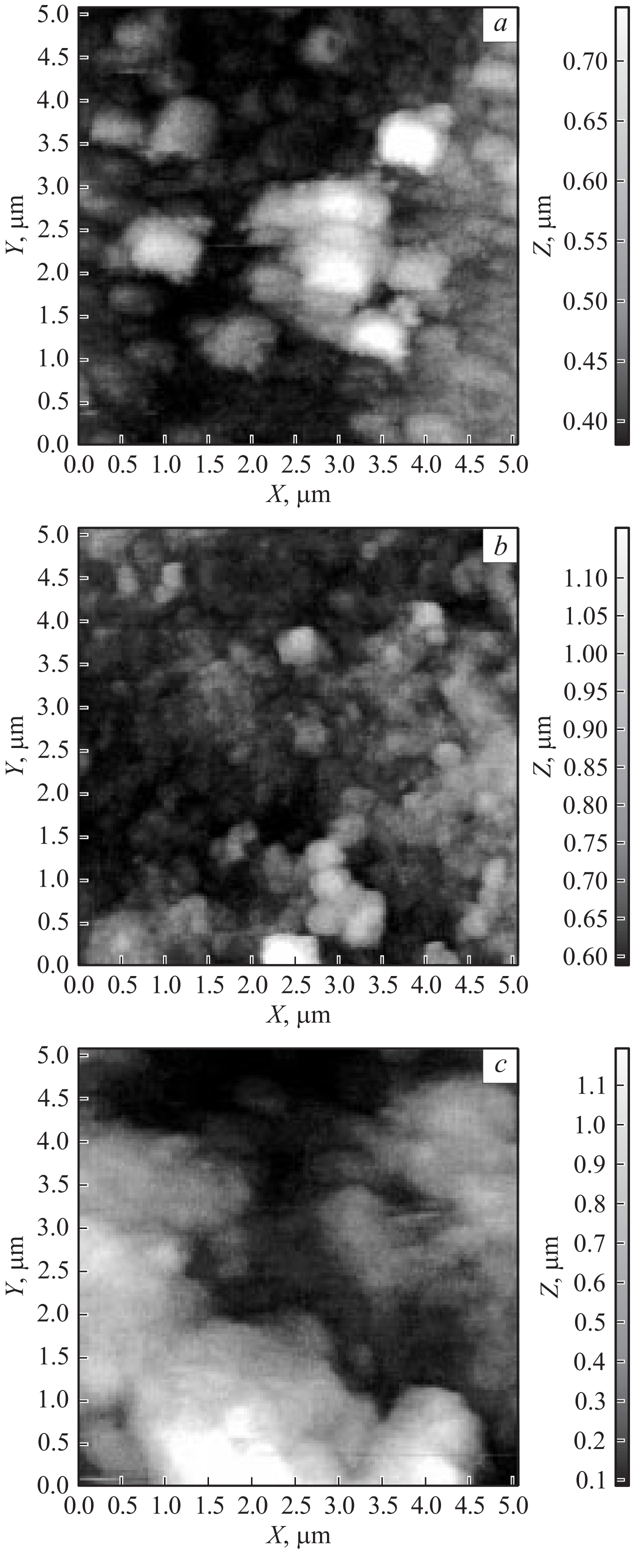

Figure 1. AFM reconstruction of surface topography of initial silica gel ShSKG (*a*) and vanadium containing (ligh orange (*b*) and red (*c*) colours) silica gel.

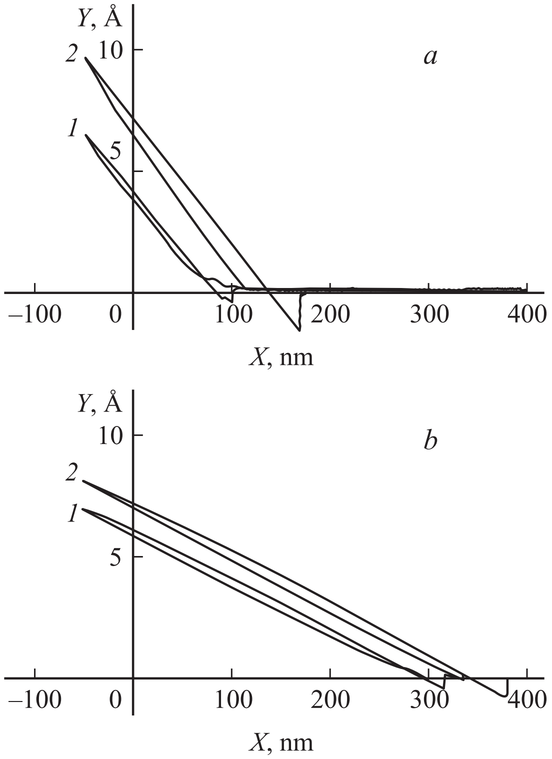

Figure 2. Force–distance curves of probe interactions for silica gels ShSKG (*a*) and IVS-1 (*b*): a_{H_2O}, mmol/g: *1* — 1.5, *2* — 4.

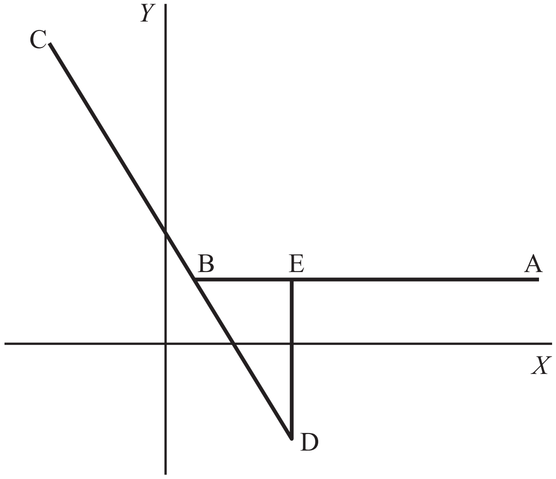

Figure 3. Model dependence (force of interacting)–distance.

Calcutaion of changes of structural characteristics of initial and vanadium containing silica gels (S_{SURF} and V_P) and thickness of adsorbate on the surface, leads to the guess of level-by-level adsorption, on a procedure [5], has shown (Fig. 4) that with increasing of quantity of adsorbate

Structural characteristics of silica gel ShSKG

Name of parameter	Label	Unit of measurement	Value
Specific surface area	S_{SURF}	m^2/g	246
Volume of pores	V_{P}	cm^3/g	0.96
Diameter of a globule*	d_0	nm	9.7
Number of globules in 1 g of a silica gel*	m_0	g^{-1}	$9.07 \cdot 10^{17}$
Number of contacts between globules*	f		3.95
Diameter of a pore*	d_{P}	nm	15.6
Diameter of a pore orifice*	d_{OR}	nm	9.5

Notice: *The data was calculated.

at surfaces down to an overlap the adsorbed stratum of a pores orifice monotonic decrease S_{SURF} and V_P of sorbent should be observed. Thickness of adsorbate, monotonously increasing at initial acts of sorption, is sharply incremented at a filling of porous and decreasing S_{SURF} up to units of m^2. However even in this case the calculated thickness of sorbed water should achieve 3.5−4.5 nm (see Fig. 4), that there is more less than the thickness of measured during local force spectroscopy of silica gels surface.

Apparently, during adsorption in dynamic regime at high temperature originating on the silica gel surface layer of water stoppers throats of pores with a meniscus, interfering with sweeping access of molecules of adsorbate to an intrapore space of a silica gel. There the surface area of the material participating in the adsorption processes considerably decreases (see Fig. 4). The opportunity of such process is confirmed also with data [10] where it is established, that the specific surface area of porous silica measured by water vapour adsorption, owing to specific interacting of carrying agent with adsorbate makes only 13−25% from real.

In case of water adsorption in static conditions (at $P/P_S = 0.85$) even at $a_{\mathrm{H_2O}} \approx 8.0$ mmol/g the thickness of H_2O spotted from local force spectroscopy data, considerably below, than certain during adsorption, and makes only 11.5−12.0 nm.

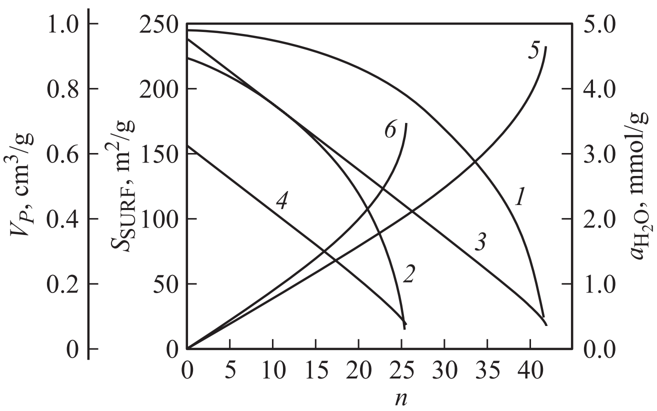

Figure 4. Calculated changes of S_{SURF} (*1, 2*), V_P (*3, 4*) and thickness of adsorbate films (*5, 6*) for ShSKG (*1, 3, 5*) and IVS-1 (*2, 4, 6*).

4. Conclusion

Thus, comparison of calculated and experimental dates allows to assume the following mechanism of H_2O adsorption in dynamic conditions at high temperature: during the adsorption of the first portions of sorbate on the silica gel surface the thin film of water overlaping the access to an intrapore space and adsorption proceeds only on an exterior surface of a sorbent.

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Редактор Т.А. Полянская