This study was focused on the release kinetics of metronidazole, decamethoxine, silver nitrate, zinc sulfate, glycine, and tryptophan into aqueous medium from the nanocomposites based on a polymer matrix filled with nanosilica or having no filler. Interpenetrating polymer network containing 83 % polyurethane (PU)/17 % poly(2-hydroxyethyl methacrylate) (PHEMA) as well as individual PU or PHEMA were used as matrix. It has been found out that including substances into the polymers together with nanosized silica considerably slows down their release. Supposedly, one of the reasons of this effect may be the interaction of the filler with the polymer network, which makes it more rigid and less penetrating. In order to check this assumption, we carried out the IR study of specially prepared samples consisting of 2-hydroxyethyl methacrylate (HEMA) and a high content of silica, by analyzing IR spectra of the obtained samples, the interaction between silica surface hydroxyl groups and carbonyl groups of HEMA.

Thus, the interaction of matrix component PHEMA with silica filler can be considered as a factor that impacts on the release kinetics of bioactive substances from examined nanocomposites.

Keywords: nanosized silica, poly(2-hydroxyethyl methacrylate), polyurethane, biologically active substanses, nanocomposites, release kinetics, IR spectra.

Матеріал надійшов 11.01.2016

УДК 544.18+544.72

V. Kaurkovska, A. Grebenyuk, V. Lobanov

EFFECT OF ADSORPTION OF SIMPLE MOLECULES ON PHASE TRANSITION IN VANADIUM DIOXIDE

The effect of adsorption of simple molecules on the temperature of phase transiton in vanadium dioxide (T = 338–339 K) has been studied by means of the models of vanadium dioxide surface commensurable with the sizes of the molecules participating in adsorption. Temperature dependences of the free energy of phases before and after the transition intersect at temperatures of 200–216 K, which is known for nanostructure of vanadium dioxide. Calculations by DFT method produce results almost identical to the calculations ab initio.

Keywords: vanadium dioxide, phase transition parameters, quantum chemistry, cluster approach.

Introduction

The phase transition of "insulator-metal" type (PTIM) in vanadium dioxide takes place at 338–340 K accompanied by hopping changes in optical and electric properties of the substance. When the temperature amounts to that of phase transition (TPT), the resistance decreases for 2–5 orders of magnitude, a structural rearrangement occurs, the volume of the unit cell decreases [1]. The phase-transition of VO_2 has been studied for years and several fundamental studies are currently being conducted for understanding the transitional process by femtosecond-transient measurements, nano-scopic imaging, etc. [2–6].

These changes are the basis for a series of optoelectronic applications. VO_2 thermochromic smart windows can regulate solar energy transmission through the window without a

noticeable visual difference by responding to ambient temperature. Thus, vanadium dioxide is a promising candidate for various thermochromic devices. Smart windows are something like thermooptical "membranes" for hot solar beams.

In the VO_2 crystalline structure, vanadium-oxygen octahedra are groupped into layers, the V-O interlayer bonds are less strong than those within the layers.

It is known that in superthin films of vanadium dioxide on silicon phase transition occurs at 100–240 K [7]. Dependence of the temperature of phase transition on the sizes of grains of a film is observed.

Earlier it has been shown that after thermal and radiation-thermal processing, VO_2 surface has a relaxation without adsorption during 1–3 hours [8]. Such a property of the surface allows us to make experiments on adsorption without preliminary pumping out, as it is accepted for oxides of the higher valences. It is experimentally shown that in steams of water the temperature of phase transition in oxide films decreases for some degrees, and in spirit – steams raises. However, there is no doubt that water adsorption on the surface has higher priority. Therefore it is necessary to understand that experimental data for alcohol cannot coincide with those of computer experiment.

In this paper we investigated the thermochemistry of adsorption of water molecules and of methanol ones on the minimum models for VO_2 surface. Surface models are commensurable with the sizes of the molecules participating in adsorption.

Methods

Ribbon-ring vanadium dioxide models have been built of 4 formula units of metallic phase (or 2 formular units of a semi-conductor phase). The basic element of the structure is a chain of O-V-O fragments. The torn off communications in model compensated atoms of hydrogen. Therefore the total formula of model $4VO_2$ ($6H_2O$).

The calculations were carried out by Hartree – Fock – Roothaan method with basis set SBKJC by means of the program package PC GAMESS [9]. For specification of results we had been carried out calculations by method of density-functional theory (DFT) with the hybrid exchange-correlation functional B3LYP.

Results and discussion

Fig. 1, *a* depicts the model of a surface which consists of four formula units. In fig. 1, *b* and *c*, models are shown where water and alcohol molecules are located over vanadium atoms. All models are presented after geometry optimisation

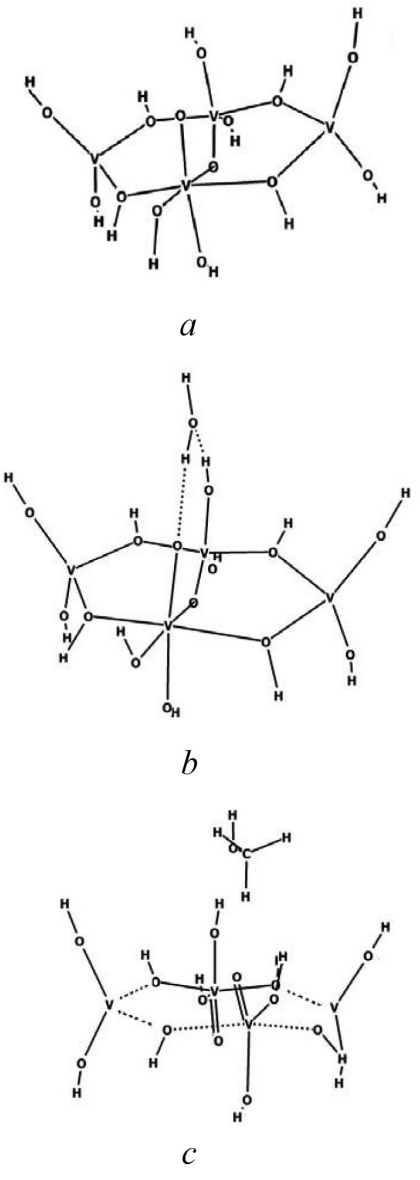

Fig. 1. Model systems: *a* – cluster of $4VO_2$ ($6H_2O$); *b* – cluster of $4VO_2$ ($6H_2O$) with a water molecule; *c* – cluster of $4VO_2$ ($6H_2O$) with a molecule of methyl alcohol CH_3OH

Water molecules and methanol ones have been approached to the surface for distance of 2–2,5 Å. Here the phase of insulator associated with a singlet state and that of metal – with a state of a higher multiplicity. Those states for model $4VO_2$ ($6H_2O$) are defined by the formula M = n + 1 where n – the number of free (unpaired) electrons, here n = 4 and M = 5.

For systems "surface – molecule (water or alcohol)" the states of the higher multiplicity have been found by means of computer experiment and aree defined as triplets.

At phase transition, there is a balance between metal and insulator. It is known that thermodynamic potentials are equal under balance condition.

Therefore it is fair to expect that the calculated values of thermodynamic parametres are to be equal at TPT.

The values of free energy ΔG as a function from temperature are presented in fig. 2. The temperature of phase transition found at approximation of functions for two states corresponding to phases of a metal and of an insulator.

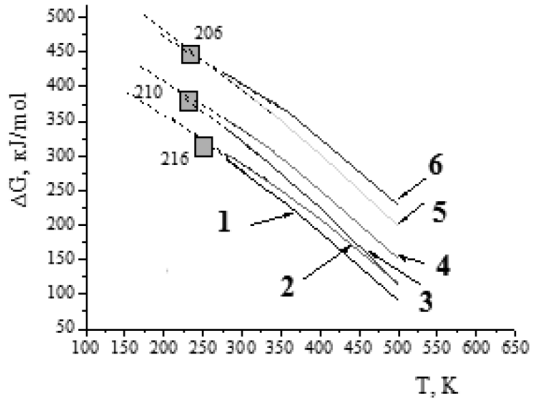

Fig. 2. Temperature dependences of free energy (Gibbs) for models "$4VO_2$ ($6H_2O$)" (*1* – singlet and *2* – quintet); "$4VO_2$ ($6H_2O$) + H_2O" (*3* – singlet and *4* – triplet); "$4VO_2$ ($6H_2O$) + CH_3OH" (*5* – singlet and *6* – triplet)

From the presented data it is seen that lines of temperature dependences ΔG for surface models are crossed at 216 K.

From fig. 2 it is seen that due to adsorption of water and methanol the temperatures of phase transition are decreased in comparison with the temperature of phase transition in parent VO_2.

The data obtained by method DFT for model VO_2 a state singlet and a quintet are presented on fig. 3. At calculations of optimum configurations of models by DFT method of distance between atoms it is a little bit more, rather than at calculation by method Hartree – Fock. However the parameters received with use of method DFT (fig. 3), differ slightly.

Though small deviations in TPT, are considered to result from the inaccuracy of the employed model

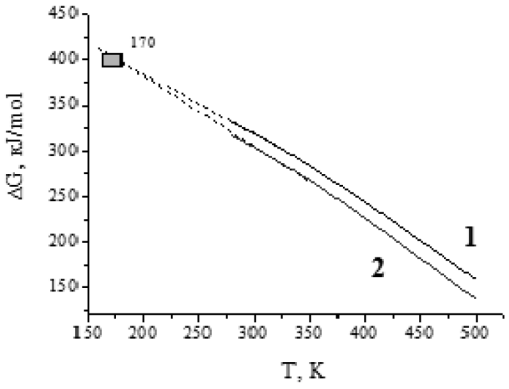

Fig. 3. Temperature dependences of free energy (Gibbs) for models "$4VO_2$ ($6H_2O$)", *1* – singlet and *2* – quintet, after calculations by DFT method

for the present analysis, there is a good coordination of the calculated parametres with literary data [7].

Calculations by method DFT give close values TPT, however speed of calculations twice it is more.

It is obvious that here the values ΔG (at the small size of model) mismatch real, and such temperatures are not characteristic for macroobjects. However, the presented results illustrate tendencies of change in temperature of the phase transition, known from the experiment.

In the present study it can be assumed that modelling of electronic phase transitions and influence of adsorption on their parametres can be realised by means of minimum models.

Conclusions

The ability to decipher of the effect of adsorption simple molecules on phase transition in vanadium dioxide is demonstrated by the results reported here. Temperatures of phase transition of the investigated systems are found in points of crossing of temperature dependences of free energy of phases before transition. Such approach has allowed to define, that area of temperatures TPT = 200–220 K. The obtained data will be co-ordinated with the literary. Calculations by method DFT give close values TPT, however speed of calculations it is much more.

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Каурковська В. М., Гребенюк А. Г., Лобанов В. В.

ВПЛИВ АДСОРБЦІЇ ПРОСТИХ МОЛЕКУЛ НА ФАЗОВИЙ ПЕРЕХІД У ДІОКСИДІ ВАНАДІЮ

Вплив адсорбції простих молекул на температуру фазового переходу (T = 338–339 K) досліджено з використанням моделей поверхні діоксиду ванадію, співвимірних із цими молекулами. Температурні залежності вільної енергії фаз до та після переходу перетинаються за температур 200–216 K, що відомо для наноструктур діоксиду ванадію. Показано, що використання методу теорії функціоналу густини з гібридним функціоналом B3LYP дає результати, майже ідентичні отриманим ab initio.

Ключові слова: діоксид ванадію, параметри фазового переходу, квантова хімія, кластерне наближення.

Матеріал надійшов 10.01.2016

УДК 544.723:544.127

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EFFECT OF NITROGEN DOPING ON THE SPATIAL AND ELECTRONIC STRUCTURE OF TIO_2 THIN FILMS AND ON THE EFFICIENCY OF WATER MOLECULES ADSORPTION ONTO THEIR SURFACES

Nitrogen incorporation into the lattice structure of titania films was proved by XPS measurements. Quantum chemical calculations were performed to find out the difference in the adsorption of water molecules onto the pure titania and nitrogen doped titania films. The effect of nitrogen doping on the values of adsorption energy of water molecules on titania species has been found, as well as a decrease in adsorption energy, which can be responsible for promotion of their photocatalytic activity The total energy values of the optimized geometrical structures of different size TiO_2 and TiO_2(N) cluster models (including 3 to 9 titanium atoms) was calculated by using the density functional theory method (DFT) and the hybrid B3LYP potential with basis set 6-31G(d, p) by means of the software package PC GAMESS (version FireFly 8.1.0 by A. Granovsky).

Keywords: nitrogen doped titania, electronic structure, XPS spectra, water adsorption, quantum chemical calculations, density functional theory method.