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Quantum-Chemical Study of Adsorption of Ag_2, Ag_4, and Ag_8 on Different Parts of the TiO_2 Surface

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Abstract—Quantum-chemical study of the adsorption of two-, four- and eight-atomic silver clusters on stoichiometric and partially reduced rutile (110) surface, and of silver tetramer on the surface of anatase (101) was carried out in the framework of periodic DFT model. The most energetically favorable positions of clusters on the surface of TiO_2 and the mechanism of binding the clusters with the substrate were revealed. According to the calculations, the adsorption of silver clusters on the surface of stoichiometric rutile (110) is more preferable than on the partially reduced one. The mechanism of binding the clusters with the surface of anatase and rutile is shown to be similar.

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Initially, an interest in the study of systems based on titanium dioxide was due to their photocatalytic activity in the decomposition of water into hydrogen and oxygen [1]. We also know that these systems may be involved into a number of other photocatalytic reactions [2]. Therewith, the systems based on the deposition on the TiO_2 surface of silver nanoparticles exhibit higher photoactivity than the individual titanium dioxide [3,4]. According to a number of studies, the best photocatalytic activity of the systems Ag/TiO_2 occurs when the average size of the deposited silver particles is 4–5 nm [5, 6]. Due to the small particle size such systems are convenient for quantum-chemical simulation. It should be noted that the quantum-chemical study of the surface of titanium dioxide, as well as features of its interaction with the metal particles have been actively carried out only in the last decade due to the appearance of new theoretical methods of calculation, as well as the development of computer technology. To date, in the literature mostly the data of theoretical calculations of the interaction of individual Au, Pt and Pd atoms with the titanium dioxide surface are available [7–13]. In this paper we calculated the adsorption energy of two-, four- and eight-atomic silver clusters with the surface of the stoichiometic and nonstoichiometric rutile (110) and anatase (101) and carried out a comparative analysis of the interaction of silver clusters with various parts of the TiO_2 surface. In order to determine the mechanism of linking the cluster with the surface, for the most stable structures are constructed the density of states diagrams (DOS), as well as graphs of the distribution of electron density for certain energy levels.

Method of calculations. Earlier [14] we showed that the adsorption energy of the silver dimer on the rutile surface calculated with the periodic model fits experimental data better than that calculated with the cluster model. Therefore in this work we used the periodic model for calculations. Calculations were performed within density functional theory (DFT) using a gradient-corrected functional PBE [15] of Espresso program [16]. As the basis set plane waves were used with the upper limit of energy (*cut-off*) 272 eV in the case of adsorption on rutile and 300 eV for anatase. We selected the ultra-soft pseudopotentials: relativistic for Ag and Ti cores and nonrelativistic for the O core [17]. An optimization of geometric parameters of all structures was carried out at the *G*-point. To assess the reliability of the used approximation we carried out a comparative calculation of the geometry and energy characteristics of the silver dimer adsorption on the rutile using the reciprocal grid of *k*-vectors 2×2×1 according to Monkhorst–Pack [18]. The calculation results were very close to those for the *G*-

point: the difference in the calculated adsorption is only 0.1 eV. Calculations of the density diagrams of the states and the graphs of electron density were performed with the basis set with the upper boundary energy 340 eV and a set of *k*-vectors 5×5×1. All calculations were performed in an approximation when the electron population of the zones corresponds to the Gaussian distribution with propagation 3.7×10^{-3} Ry.

As a model of the rutile surface (110) we used three-layer structure consisting of nine atomic layers. The lower layer, whose geometrical parameters are consistent with experimental data [19], remained "frozen" (its geometry remained unchanged at optimization), and two top layers were optimized. In the calculations we used the rutile 6×1 surface unit cell with the translation vectors directed along the diagonals of the 3×1 surface cell. This direction was chosen to minimize the lateral interactions between the neighboring adsorbed clusters. The distance between the neighboring layers was 20 Å. At the simulation of the nonstoichiometric surface, one bridging oxygen atom on the upper layer was removed. This model reproduces the surface of rutile with the concentration of oxygen vacancies 16.7%. In the case of anatase, the surface unit cell consisted of 12 atomic layers, therewith four lower layers were frozen. In the framework of our model 3×2 surface was used with the translation vectors directed along the diagonals of the cell 2×2 and 1×2.

The calculations were performed only for the singlet electronic states. However, in the case of the surface of nonstoichiometric rutile (110) a calculation was additionally carried out of the triplet state energy. The resulting energy difference between triplet and singlet states was only 0.07 eV. Such a small difference is due to the strong delocalization of the unpaired electrons of vacancies on the adjacent atoms [20].

Adsorption of silver clusters on the stoichiometric rutile (110) surface. The stoichiometric surface of rutile (110) consists of the chains of bicoordinated bridging oxygen atoms O(2c) associated with hexacoordinated titanium atoms Ti (6c), as well as the atoms in the hollows between the O(2c) chains: pentacoordinated titanium atoms Ti(5c) and tricoordinated oxygen atoms O(3c). Thus, the surface has two principal sites for adsorption: over the atoms O(2c) and over the atoms in the hollows. We have investigated the structures corresponding to the adsorption of silver clusters both on O(2c) and over atoms in the hollows. The most stable isomers of the silver tetramer and octamer were chosen for the calculations: the rhombic isomer of Ag_4 [21] and the D_{2d} structure in the case of Ag_8, consisting of two deformed rhombs, one above the other and rotated by 45º to each other [22].

To determine the most energetically favorable positions of the adsorbed Ag_2, Ag_4, and Ag_8 clusters on the TiO_2 surface we carried out the optimization of the geometric parameters of 20 different starting structures. Figure 1 shows the most stable structures obtained by optimization, as well as the calculated values of adsorption energy and the total charge of the adsorbed cluster. As seen from Fig. 1, the adsorption of clusters in the hollows is energetically more favorable. The energy of adsorption for the most stable structures of Ag_2/TiO_2, Ag_4/TiO_2, and Ag_8/TiO_2 is 1.17, 1.97, and 1.85 eV, respectively. It should be noted that these results agreed well with the experimental data on the deposition of small silver clusters on the rutile (110) surface [23, 24], which showed that the adsorption of particles in the hollows is preferable.

To determine the mechanism of binding the silver clusters with the rutile surface, we have constructed the state density diagrams for the most stable structures, as well as for the structure corresponding to the adsorption of Ag_4 over the bridging atoms O(2c) (Fig. 2). Figure 2 shows for each structure a total and a projected for the silver cluster DOS-diagram. The calculations showed that the conduction band of rutile is mainly formed by vacant *d*-orbitals of the Ti atoms, while valence zone is filled with the orbitals of oxygen atoms. Fig. 2 also shows the graphs of the electron density for the eigenstates near the Fermi level, in which the contribution of silver is the most significant. As seen from the DOS-diagrams, in the case of adsorption of the silver dimer, these eigenstates are in the forbidden zone and their energies are about 0.01 eV, while for the most stable structures of the adsorbed silver tetramer and octamer they are near the lower boundary of the conduction band, with the energies 1.61 eV and 2.33 eV, respectively. Comparing the graphs of the electron density of these eigenstates with the shapes of the highest occupied molecular orbitals (HOMO) calculated for the individual clusters with the same geometrical parameters (Fig. 3), we can conclude that the considered energy levels are formed by the overlap of the HOMO of the cluster of silver with vacant *d*-orbitals of the Ti(5c) atoms. As a result of such overlap a partial charge transfer occurs from the cluster to the substrate. Therefore, all the adsorbed clusters have a positive

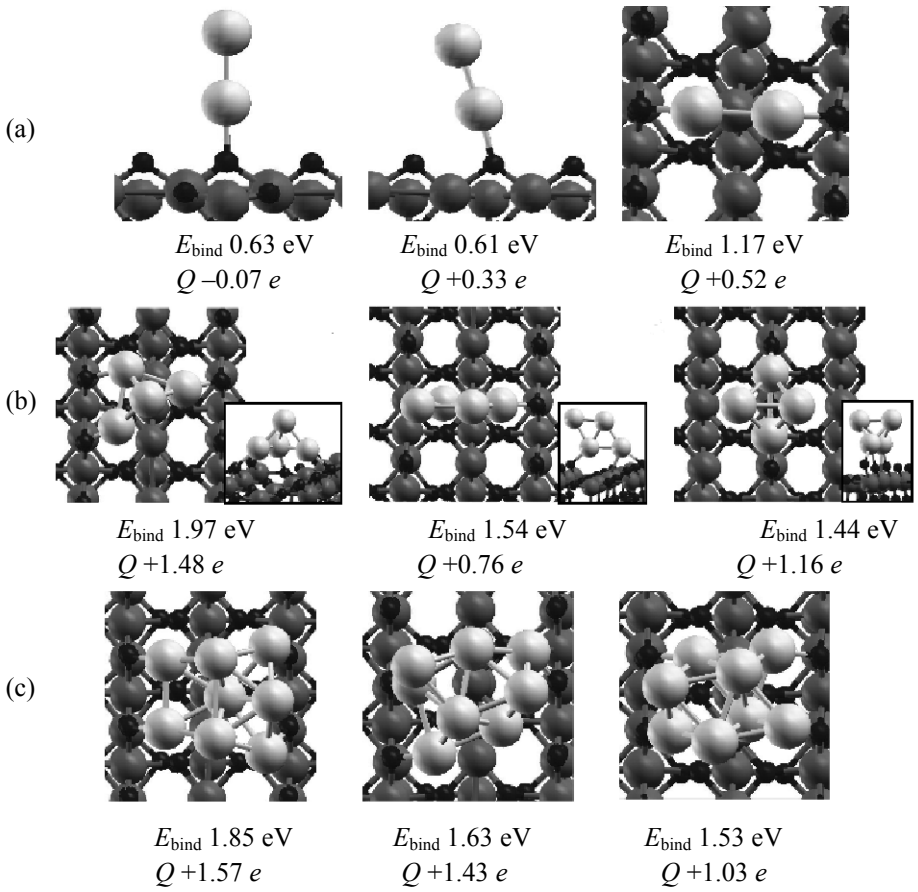

Fig. 1. Structures of silver clusters adsorbed on the surface of stoichiometric rutile (110) (a) Ag_2/TiO_2, (b) Ag_4/TiO_2, and (c) Ag_8/TiO_2. Under each structure the value of adsorption energy (E_{bind}) is shown and the charge of the adsorbed cluster (Q). Bright areas are the silver atoms, small dark are oxygens, large dark are titanium atoms.

charge (Fig. 1). Figure 2a shows also the graph of electron density for the eigenstate with energy –1.28 eV, with high enough contribution of silver orbitals. A comparison of Fig. 2a and Fig. 3 shows that to this state contribute mainly the HOMO–1 of the silver dimer and the orbitals of O(2c) atoms. Moreover, the HOMO–1 of the dimer is partially deformed to maximize the overlap with the orbitals of oxygen. We showed that such interaction is typical also for the silver clusters with a greater number of atoms. Moreover, just the overlap of orbitals of the cluster with the orbitals localized on the O(2c) atoms leads to a noticeable deformation of the silver cluster structure at adsorption (Fig. 1). The energy of this interaction as we have estimated in the previous works is comparable with the interaction energy of the first type (the HOMO of the silver cluster – the Ti(5c) vacant *d*-orbitals) [14, 25].

At the adsorption of silver clusters over the bridging oxygen atoms the overlap of the cluster HOMO with the Ti(5c) *d*-orbitals is impossible (Fig. 1). Fig. 2c illustrates the density of states for the most stable structure corresponding to the adsorption of Ag_4 over the bridging oxygen atoms, as well as the graph of the electron density for the eigenstate with the energy 1.36 eV. As seen, the location of energy levels in the DOS-diagram is similar to that in the structures corresponding to the adsorption of silver in the tetramer hollows, but the level with energy 1.36 eV is formed mainly by the HOMO of the cluster Ag_4 and almost does not overlap with the eigenstates of the substrate. The lack of overlap with the orbitals of oxygen atoms is due to the fact that energy of the latter (corresponding to the lower boundary of valence zone) is considerably lower than the energy of the silver tetramer HOMO (that corresponds to the lower

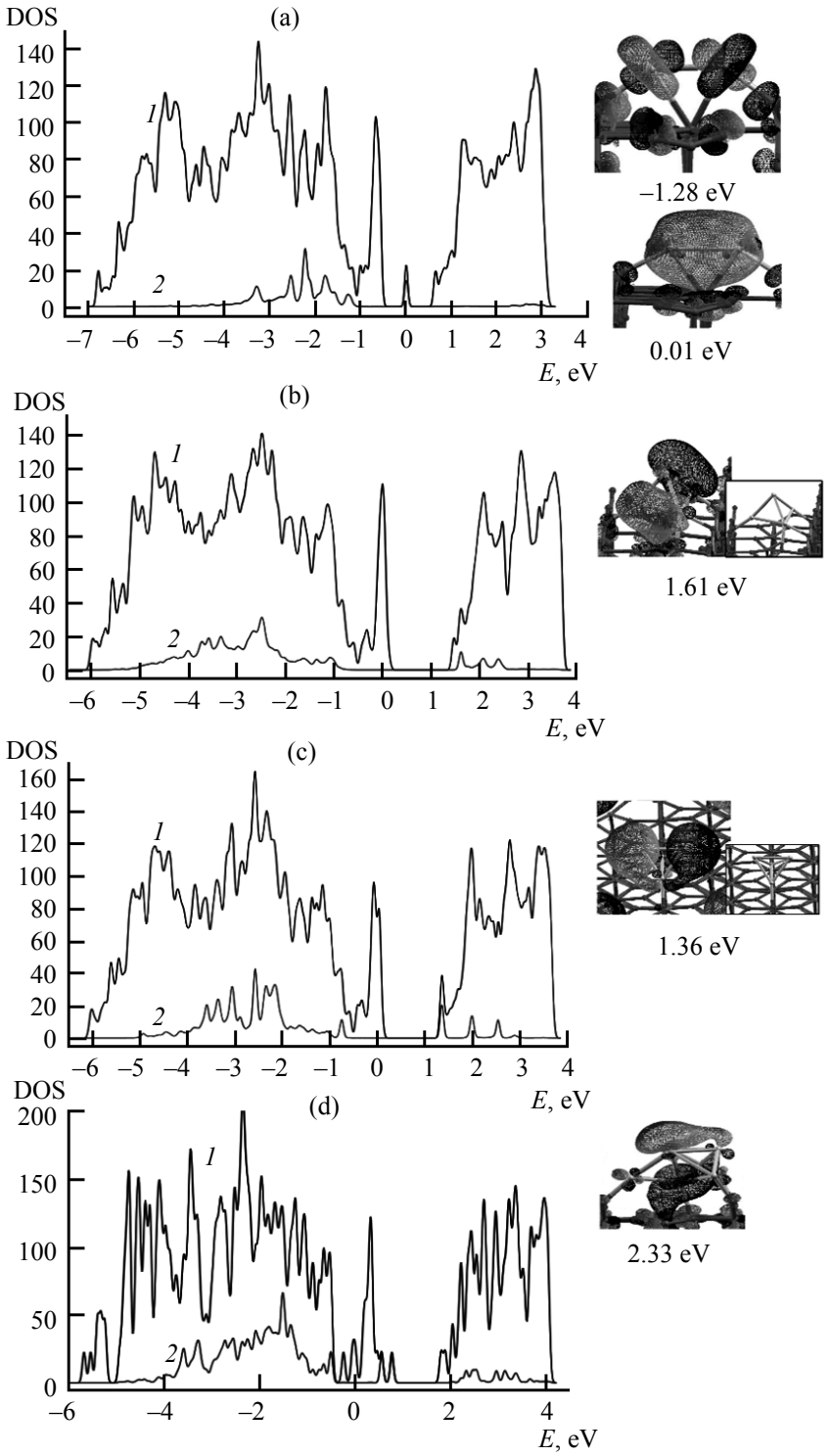

Fig. 2. Diagrams of the density of states (DOS): (*1*) total and (*2*) projected for the silver clusters, and the graphs of the distribution of electron density for some of the energy levels and structures (a) Ag_2/TiO_2, (b), (c) Ag_4/TiO_2, and (d) Ag_8/TiO_2.

boundary of the conduction band). However, the MOs of the silver cluster with lower energy are involved in the overlap with the orbitals of the atoms O(2c). Just as in the case of adsorption of silver clusters in the hollow, this interaction leads to a strong distortion of the cluster geometry (from rhombic in the case of the gas phase to tetrahedral) at the adsorption. Thus, the interaction of the silver cluster MOs with the orbitals

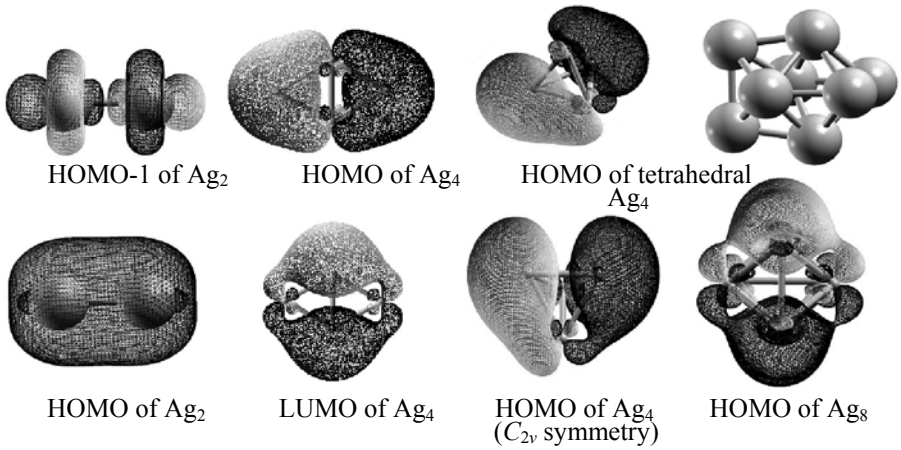

Fig. 3. Calculated shapes of selected orbitals of Ag_2, Ag_4, and Ag_8 clusters.

of the O(2c) atoms occur only in the case of adsorption over the bridging oxygen atoms. As a consequence, the adsorption energy in this case is lower than in the hollows, which is consistent with experimental data [23, 24].

Adsorption of silver clusters on the nonstoichiometric rutile (110) surface. The most widespread defect on the rutile (110) surface is the oxygen vacancy. When bridging oxygen atom is removed from the surface, two titanium atoms with unpaired electrons (Ti*) remain at the vacancy. Taking into account that the energy difference of singlet and triplet states calculated by us is small (approximately 0.07 eV), to reduce the consumption of computer time we performed calculations of the adsorption of silver clusters on the nonstoichiometric surface for the singlet state.

We carried out geometry optimization of 22 starting structures corresponding to the adsorption of Ag_2, Ag_4, and Ag_8 on the rutile surface containing oxygen vacancies. The initial structures were constructed so that the adsorbed cluster is located either directly above the vacancy, or near it. Figure 4 shows the most stable structure obtained by geometry optimization, as well as the calculated adsorption energies and the total charge of the adsorbed cluster. Calculated values of adsorption energy of most stable Ag_2/TiO_2, Ag_4/TiO_2, and Ag_8/TiO_2 structures are 0.99, 1.21, and 1.25 eV, respectively. It should be noted that these values are lower than in the case of adsorption on the stoichiometric surface. Thus, the adsorption of silver clusters on the stoichiometric regions of the TiO_2 (110) surface is preferable compared to the regions of the surface containing vacancies.

As in the previous case, to establish a mechanism of linking the cluster with the surface, we calculated the DOS-charts and graphs of electron density (Fig. 5) for a number of structures: Ag_2/TiO_2 with adsorption energy 0.84 eV, in which the cluster is located directly above the vacancy between the two bridging oxygen atoms, the structures Ag_4/TiO_2 and Ag_8/TiO_2 characterized by the highest adsorption energy (1.21 and 1.25 eV, respectively).

The density diagram of the Ag_2/TiO_2 structure (Fig. 5a) is similar to the diagram constructed for the silver dimer on the stoichiometric surface (Fig. 2a). Since the Fermi level for this structure is located at the boundary of the conduction band, the eigenstate with the energy 0.48 eV is populated. The diagram of electron density distribution for this state is shown in Fig. 5a. Comparing this graph with the HOMO of Ag_2 (Fig. 3), we can conclude that the eigenstate is formed by a cluster of silver and HOMO orbitals localized on the Ti* atoms. However, due to the fact that the energy of the orbitals of titanium atoms is higher by 0.48 eV, their own contribution to this state is small, as is evident from the DOS-diagram. Therefore, the interaction of silver clusters and the HOMO orbitals localized on the Ti* atoms is poor. Fig. 5a also shows the graph of electron density distribution for the eigenstate with the energy –1.11 eV. To this state contribute mainly the HOMO-1 of the silver dimer and the orbitals of the bridging oxygen atoms. Thus, there is an analogy with the above case of adsorption of clusters on the stoichiometric surface.

In both cases of adsorption of the silver tetramer and octamer, the cluster, due to its rather large size, is located over the vacancy, and partly over the Ti(5c)

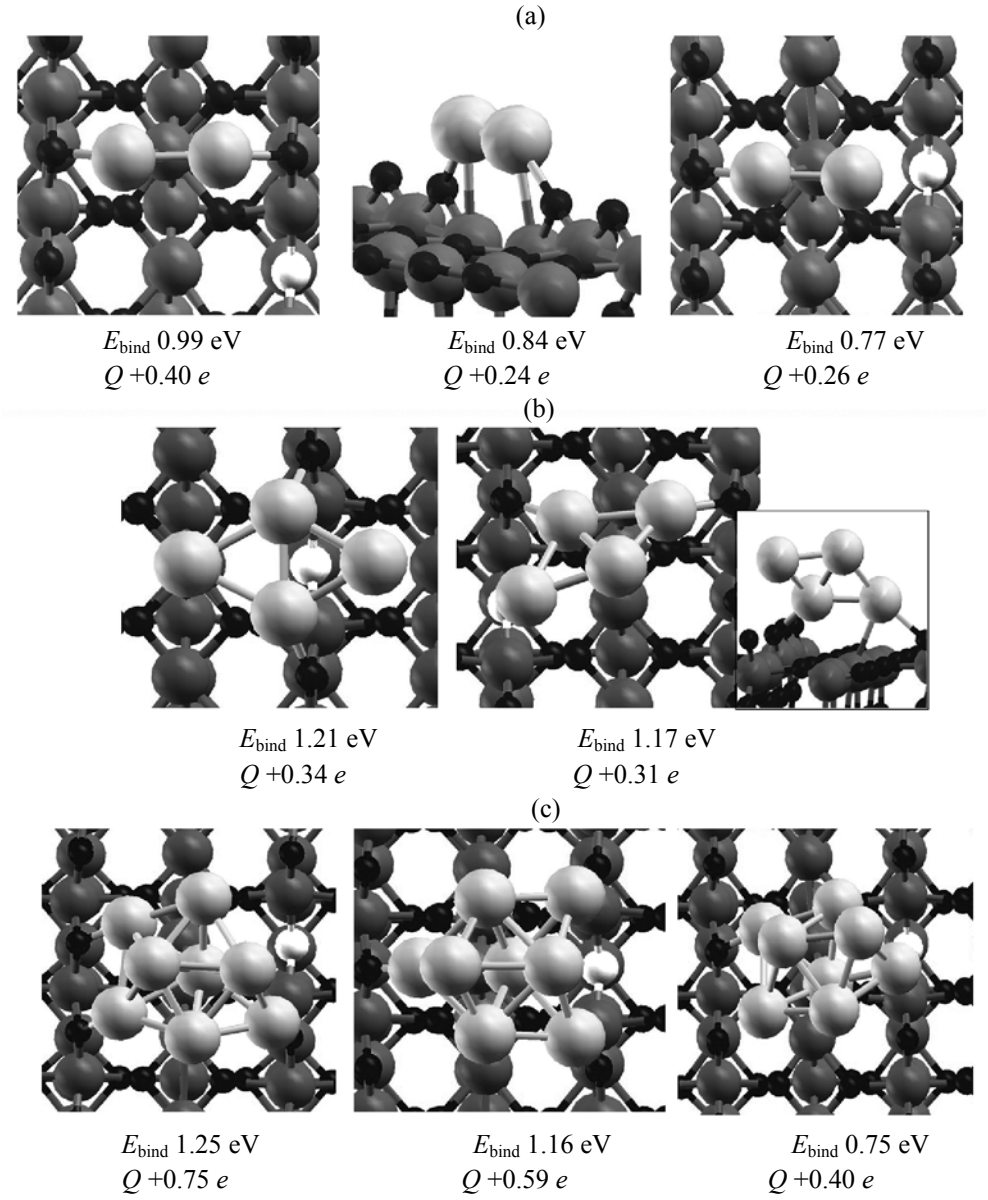

Fig. 4. Structures of silver clusters adsorbed on the surface of nonstoichiometric rutile (110). (a) Ag_2/TiO_2, (b) Ag_4/TiO_2, and (c) Ag_8/TiO_2. Under each structure the value of adsorption energy (E_{bind}) is shown and the charge of the adsorbed cluster (Q). (Bright areas) are the silver atoms, small dark are oxygens and (large dark) are titanium atoms.

atom (Figs. 4b and 4c). Analysis of the DOS-charts and the electron density graphs of the levels lying at the edge of the conduction band shows that in both cases there is an overlap of the cluster HOMO with the Ti(5c) *d*-orbitals (Figs. 5b and 5c). However, as can be seen from the DOS-charts, the contribution of the Ti* atomic orbitals to these eigenstates is much less than the contribution of Ti(5c) in the respective states at the adsorption on the stoichiometric surface. This result originates from the high energy difference of the Ag_n HOMO and the Ti* *d*-orbitals (Fig. 5). As in the case of adsorption on the stoichiometric surface, the overlap of the adsorbed cluster MOs with the orbitals of the bridging oxygen atoms leads to a distortion of the structure of the cluster.

Despite the similarity of mechanisms of binding in the case of adsorption of silver clusters on the stoichiometric and nonstoichiometric surfaces, the difference in binding energies is quite large. This signi-

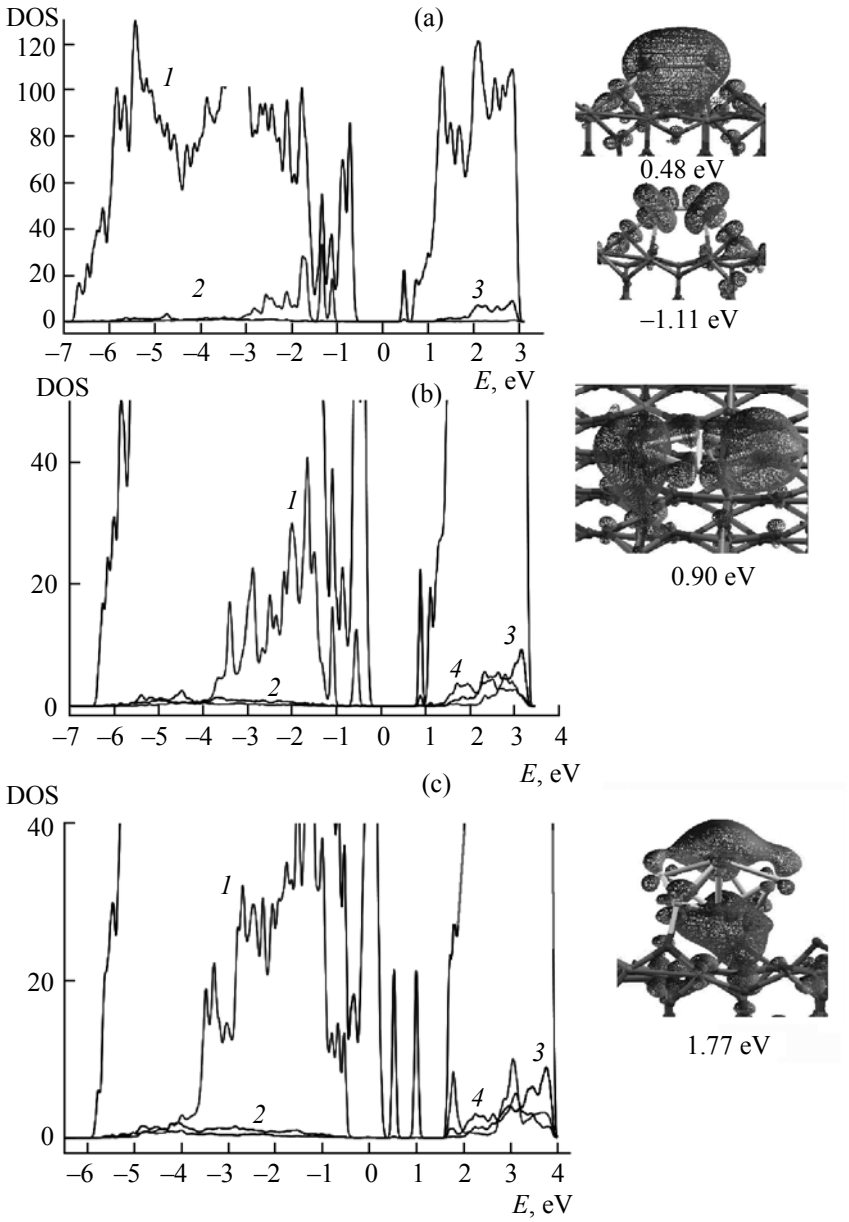

Fig. 5. Diagrams of the density of states (DOS): (*1*) total, (*2*) projected for the silver clusters, (*3*) projected for the Ti* atoms, and (*4*) projected for the Ti(5c) atoms, and the graphs of the distribution of electron density for some of the energy levels of the structures of silver clusters adsorbed on the surface of nonstoichiometric rutile (110): (a) Ag_2/TiO_2, (b) Ag_4/TiO_2, and (c) Ag_8/TiO_2.

ficant difference can originate from the fact that in all the cases there is an overlap of the Ag_n HOMO and the Ti(5c) *d*-orbitals. Due to formation of a vacancy, the energy of the Ti(5c) *d*-orbitals should increase, and the interaction of these orbitals with the Ag_n HOMO should weaken. This is indicated indirectly by a lower value of the positive charge of the adsorbed Ag_n cluster near a vacancy, compared with that in the case of adsorption on the stoichiometric surface. Thus the adsorption of silver clusters, as well as the growth of nanoparticles in the initial stages, is more likely to occur away from the oxygen vacancies on the stoichiometric regions of the surface (110).

Adsorption of Ag_4 on the anatase (101) stoichiometric surface. The surface of anatase (101) is the most thermodynamically stable, so we have chosen it for research. This surface consists of titanium and oxygen atoms with different coordination environments [Ti(5c), Ti(6c), O(2c), and O(3c)] and is of a

stepped structure. We carried out the optimization of geometric parameters of eight different structures corresponding to the adsorption of silver tetramer on the different positions on this surface. Geometric parameters and adsorption energy for the four most stable structures are shown in Fig. 6. As seen, the calculated binding energy of Ag_4 with the surface is fairly close for all the structures and have values in the range from 0.71 to 1.14 eV. In contrast to the adsorption on rutile, the geometric structure of the clusters adsorbed on the anatase surface is almost the same as that of Ag_4 in the gas phase. An exception is the structure shown in Fig. 6d, in which the geometric parameters of the adsorbed Ag_4 differ significantly from those of the individual silver tetramer. To exclude the possible influence of the lateral interaction of adsorbed clusters, we carried out an additional calculation with a larger size of the unit cell surface (4 × 2) for the structure shown in Fig. 6d. However, the results of calculation were similar to the discussed above.

For the most stable 6a structure the DOS-charts and graphs of the electron density of some of the eigenstates were calculated (Fig. 7). As seen from Fig. 7, the eigenstates, to which significantly contribute the orbitals of the silver cluster, are predominantly in the valence and forbidden zones. As in the case of adsorption on rutile, here is the level adjacent to the Fermi energy, and located at the edge of the conduction band. To this level corresponds an energy of 0.23 eV. From the analysis of the graph of electron density follows that these states are formed mainly due to the overlap of the Ag_4 HOMO with the *d*-orbitals of Ti(5c) atom. Note that similar results were obtained at the calculation of adsorption on rutile. Just as in the case of adsorption on rutile, to the states lying at the upper edge of the valence zone contribute the occupied MOs of the silver cluster and the *p*-orbitals of the bridging oxygen atoms. This can be seen from the graph of electron density of the eigenstate with energy –2.03 eV (Fig. 7).

Thus, the mechanism of binding small clusters of silver with the surface of titanium dioxide is identical for the two modifications of TiO_2. In the case of adsorption on anatase the interaction of the cluster MOs with the orbitals of the atoms O(2c) is weaker compared with adsorption on the (110) rutile surface. Apparently this is the main reason for lower value of adsorption energy of silver clusters on the anatase.

Thus, in this research we have studied the adsorption of clusters Ag_n (n = 2, 4, 8) on the surface

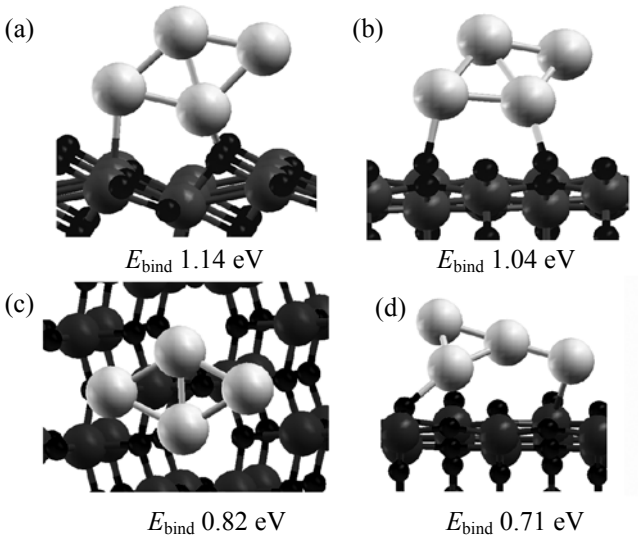

Fig. 6. Some structures of the Ag_4 clusters adsorbed on the surface of stoichiometric anatase (101). Under each structure the value of adsorption energy (E_{bind}) is shown and the charge of the adsorbed cluster (Q). (Bright areas) are the silver atoms, small dark are oxygens and (large dark) are titanium atoms.

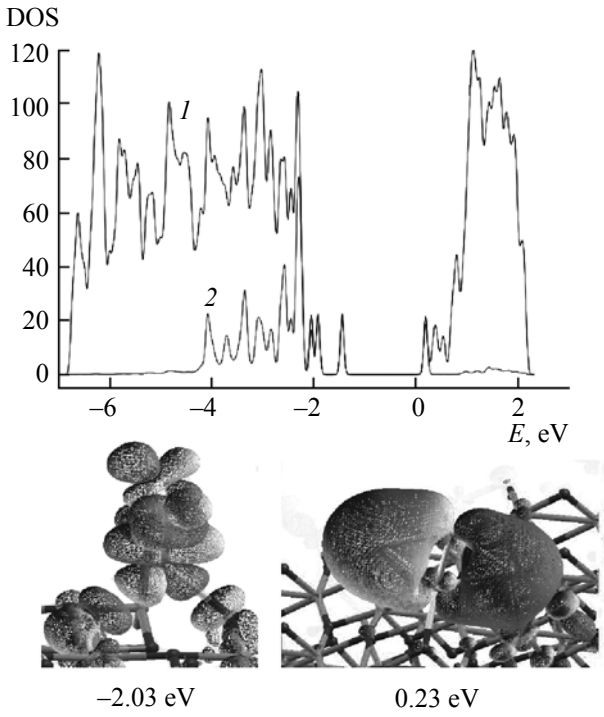

Fig. 7. Chart of the density of states (DOS): (*1*) total and (*2*) projected for the silver clusters, and the graphs of the distribution of electron density for some of the energy levels of the structure shown in Fig. 6a.

of stoichiometric and nonstoichiometric rutile (110), as well as on the stoichiometric surface of anatase (101), and revealed the energetically most favorable positions of adsorbed cluster, calculated binding energy and investigated the mechanism of binding the cluster with the surface.

It is shown that at the adsorption of the silver clusters on the rutile (110) surface, mainly two types of interaction contribute to the binding. First of all, it is the interaction of the cluster HOMO with the vacant *d*-orbitals of the pentacoordinated titanium atom lying in the hollow between the rows of the bridging oxygen atoms. As a result of this interaction the electrons are transferred from the HOMO of the cluster on the vacant *d*-orbitals of titanium, which leads to a partial positive charge on the adsorbed silver clusters. On the other hand, there is overlap between the occupied molecular orbitals of the cluster and the orbitals of the bridging oxygen atoms. The presence of the second type of interaction causes a deformation of the silver cluster at the adsorption.

According to the calculations, the most preferred surface regions for the adsorption of silver clusters are the hollows between the bridging oxygen atoms, because in this case the interactions of both types are acting, whereas at the adsorption on the bridging oxygen atoms the overlap of the cluster HOMO with the Ti *d*-orbitals is impossible.

We showed that the adsorption on the surface of nonstoichiometric rutile is less preferable than on the stoichiometric one. Binding the cluster over the vacancies is rather weak, since the energy difference between the Ag_n HOMO and the unsaturated titanium atom *d*-orbitals is quite large. The reduced contribution of this type of interaction at the adsorption on the nonstoichiometric surface diminishes the positive charge on the adsorbed silver clusters. Therefore we can conclude that the adsorption of silver clusters should most likely occur on the regions of the stoichiometric rutile (110) surface away from the oxygen vacancies.

We showed that the mechanism of binding the cluster with the anatase surface is very similar to that of the adsorption on rutile. However, the interaction of the cluster MOs with the bridging oxygen atoms in the case of anatase is weaker, which results in lower values of adsorption energy at the adsorption of the silver clusters on anatase.

Analysis of the DOS-charts shows that the most of the examined systems have occupied energy levels in the forbidden zone, localized on the adsorbed silver clusters, and with an increase in the number of atoms in the cluster the density of levels in the forbidden zone increases. Thus, at the absorption of a photon, the charge carriers will appear on the surface. This may cause higher photocatalytic activity of systems Ag/TiO_2 compared with the individual TiO_2 [3].

REFERENCES

1. Fujishima, A. and Honda, K., *Nature*, 1972, vol. 238, p. 37.
2. Diebold, U., *Surf. Sci. Rep*., 2003, vol. 48, p. 53.
3. Tran, J.S., Chiang, K., and Amal, R.J., *J. Photochem. Photobiol., A: Chem*., 2006, vol. 183, p. 41.
4. Shchukin, D., Ustinovich, E., Sviridov, D., and Pichat, P., *Photochem. Photobiol. Sci*., 2004, vol. 3, p. 142.
5. Feldhoff, A., Mendive, C., Bredow, T., and Bahnemann, D., *Chem. Phys. Chem*., 2007, vol. 8, p. 805.
6. Grünert, W., Bruckner, A., Hofmeister, H., and Claus, P., *J. Phys. Chem., B*, 2004, vol. 108, p. 5709.
7. Chrétien, S. and Metiu, H., *J. Chem. Phys*., 2007, vol. 127, p. 084704.
8. Chrétien, S. and Metiu, H., *J. Chem. Phys*., 2007, vol. 127, p. 244708.
9. Vittadini, A. and Selloni, A., *J. Chem. Phys*., 2002, vol. 117, p. 353.
10. Han, Y., Liu, C.-J., and Ge, Q., *J. Phys. Chem., B*, 2006, vol. 110, p. 7463.
11. Zhang, J., Zhang, M., Han, Y., Li, W., Meng, X., and Zong, B., *J. Phys. Chem., C*, 2008, vol. 112, p. 19506.
12. Pacchioni, G.G., Bredow, T., and Sanz, J.F., *Surf. Sci.,* 2001, vol. 471, p. 21.
13. Pillay, D, Wang, Y., and Hwang, G.S., *Catal. Today*, 2005, vol. 105, p. 78.
14. Mazheika, A.S., Matulis, V.E., and Ivashkevich, O.A., *J. Mol. Str. (Theochem.)*, 2010, vol. 942, p. 47.
15. Perdew, J.P., Burke, K., and Ernzerhof, M., *Phys. Rev., B,* 1996, vol. 54, p. 16533.
16. Baroni, S., Dal Corso, A., de Gironcoli, S., Giannozzi, P., Cavazzoni, C., Ballabio, G., Scandolo, S., Chiarotti, G., Focher, P., Pasquarello, A., Laasonen, K., Trave, A., Car, R., Marzari, N., and Kokalj, A., *www.pwscf.org*.
17. Vanderbilt, D., *Phys. Rev., B*, 1990, vol. 41, p. 7892.
18. Monkhorst, H.J. and Pack, J.D., *Phys. Pev., B*, 1976, vol. 13, p. 5188.
19. Charlton, G., Howes, P.B., Nicklin, C.L., Steadman, P., Taylor, J.S.G., Muryn, C.A., Harte, S.P., Mercer, J., McGrath, R., Norman, D., Turner, T.S., and Thornton, G., *Phys. Rev. Lett*., 1997, vol. 78, p. 495.

20. Vilay, A., Mills, G., and Metiu, H., *J. Chem. Phys*., 2003, vol. 118, p. 6536.
21. Matulis, V.E., Ivashkevich, O.A., and Gurin, V.S., *J. Mol. Struct. (Theochem.)*, 2003, vol. 665, p. 291.
22. Zhao, G.F., Lei, Y., and Zeng, Z., *Chem. Phys.,* 2006, vol. 327, p. 261.
23. Tong, X., Benz, L., Chrétien, S., Kemper, P., Kolmakov, A., Metiu, H., Bowers, M.T., and Buratto, S.K., *Chem. Phys.,* 2005, vol. 123, p. 204701.
24. Tong, X., Benz, L., Kolmakov, A., Chrétien, S., Metiu, H., and Buratto, S.K., *Surf. Sci*., 2005, vol. 575, p. 60.
25. Mazheika, A.S., Matulis, V.E., and Ivashkevich., O.A., *J. Mol. Struct. (Theochem.)*, 2009, vol. 909, p. 75.